

**A Validation Study at the EERC of the
Fluegas Mercury Sorbent Speciation or
FMSS Method**

FMSS Speciation Method - Performance Based Measurement System (PBMS)

Outline of document to satisfy the PBMS requirements

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I. Abstract

An analytical study, using the guidelines of the US EPA Performance Based Measurement System (PBMS) was completed for the Fluegas Mercury Sorbent Speciation (or FMSS) Method. The FMSS method uses a semi-isokinetic sampling approach with a mini-particulate filter in the fluegas duct followed by a heated solid sorbent sample train to selectively determine particulate Hg (PHg), gaseous oxidized Hg (Hg^{+2}) and elemental Hg (Hg^0) and the sum of species, total Hg (THg). The analysis of the FMSS samples is done after appropriate strong acid digestion using cold vapor atomic fluorescence spectroscopy (CVAFS) using EPA Method 1631B (modified). The justification for this study is twofold: first the FMSS method has distinct advantages over the currently employed impinger method for use in emission and Hg control studies and secondly may be desirable for continuous emission monitor (CEM) development and then ongoing quality assurance performance evaluation. The intent of the PBMS approach to validation of a method is to define and determine under real conditions the scope, quality control requirements, method detection limit, ruggedness, accuracy, precision, interferences, matrix suitability and laboratory reproducibility. All aspects of the PBMS analytical protocol were addressed in this study. The majority of the PBMS was conducted at the University of North Dakota's Energy and Environmental Research Center Pilot Plant. Another study of the FMSS was completed at the US Department of Energy Pilot Plant, with similar results, but is not summarized here. Most importantly, all FMSS Method sample runs were collected in parallel with the ASTM approved Ontario Hydro (OH) Method. The study was conducted using various fuels, two types of particulate control devices, selective fluegas Hg species spiking and both sample flow rate and temperature variations. For all tests, at least a duplicate FMSS and OH sample were collected, and frequent quadruplicate samples were collected for the FMSS.

The FMSS method was evaluated relative to the Ontario Hydro (OH) Method at the Energy and Environment Research Center (EERC) and again at the US DOE for a variety of fuels, ash loadings, and pollution control methods. FMSS method detection limits or MDLs for coal combustion fluegas are reported (in $\mu\text{g}/\text{m}^3$) to be 0.006 for PHg, 0.027 for Hg^0 , 0.0251 for Hg^{+2} , and 0.045 for THg. The FMSS method exhibited good precision with a mean relative percent difference (RPD) of, $\pm 8\%$ for Hg^{+2} , $\pm 10\%$ for THg, $\pm 6.5\%$ for $\%\text{Hg}^{+2}$ (as the percent Hg^{+2} of the total vapor and particulate phases) $\pm 22\%$ for Hg^0 and $\pm 47\%$ for PHg. The precision values for Hg^0 and PHg were greater than the other species due to the very low concentrations measured, not inherent method or laboratory problems. Good agreement was observed between the means of the FMSS and OH method runs, with accuracy at $100 \pm 20\%$ for all species and a mean of 97% for THg and $\%\text{Hg}^{+2}$.

Based on the results of this PBMS, we conclude the FMSS Method is equivalent to the ASTM approved OH Method and a therefore a valid method for the determination of total Hg, PHg, gaseous Hg^{+2} and Hg^0 concentrations in fluegas matrices. Considering many factors, including simplicity, lack of hazardous solutions in the field, precision, sensitivity, accuracy and cost, the FMSS method has many advantages that make it a viable choice for the measurement of fluegas Hg speciation.

II. Scope and Application

The scope is to subject the Frontier Fluegas Mercury Sorbent Speciation (FMSS) Method to a full Performance Based Measurement System (PBMS) analytical study. Why is the PBMS approach being used to validate the FMSS Method? In short, the EPA Office of Solid Waste strongly supports and is committed to the agreement by the EPA's Environmental Monitoring Management Council (EMMC), with members of the regulatory community and with Congress, that changes must be made in the way monitoring requirements are specified in regulations and in permits (<http://www.epa.gov/SW-846/pbms.htm>). The PBMS approach satisfies this desired change and there is broad acceptance for its application.

The EPA defines PBMS as a set of processes wherein the data needs, mandates, or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those needs in a cost-effective manner. The flexibility of PBMS extends to publication, where there is no set document type required to communicate the criteria. The primary benefit of PBMS to both regulators and the regulated community is flexibility in method selection including: 1) Expedited approval of new and emerging technologies to meet mandated monitoring requirements and 2) Development and use of cost-effective methods that meet program requirements and their associated performance criteria. As stated by the EPA, "where PBMS is implemented, the regulated community will be able to select an appropriate analytical method... including a method not found in EPA-published manuals that is cost-effective and meets the particular project criteria".

The outcome of this study is to determine if the FMSS method is an acceptable and cost-effective method for the measurement of total and speciated mercury (particulate Hg, gaseous Hg(II) and elemental Hg) in coal fluegas. It is expected that the FMSS method will be applicable to other fluegas matrices, such as from municipal waste incinerators, sewage sludge incinerators, smelting and other high temperature or combustion processes. However, the limitations of this study are for coal fluegas only.

The principle of the FMSS method has been described previously in Prestbo and Bloom (1995) and Prestbo and Tokos (1997). The FMSS method uses a semi-isokinetic sampling approach with a mini-particulate filter in the fluegas duct followed by a heated solid sorbent sample train to selectively determine particulate Hg (PHg), gaseous oxidized Hg (Hg^{2+}) and elemental Hg (Hg^0) (Figure 1). The FMSS method uses dual dry sorbent traps for the gas phase Hg species capture with the first trap consisting of KCl coated quartz chips and the second trap containing tri-iodine impregnated activated carbon. The sampled fluegas pulled by vacuum at 0.5 liters/minute through the sample train separates in order of the traps, particulate Hg (PHg), gaseous Hg^{2+} physi-sorbed on the KCl/quartz trap and finally chemi-sorption of Hg^0 on the iodinated carbon trap. An inlet nozzle is used and its inner diameter is chosen so that the sample is collected isokinetically by matching the nozzle velocity with the fluegas velocity in the duct. The mini-particulate filter consisting of a small quartz-fiber filter disk is inserted into a quartz tube on a pure nickel support screen to collect flyash for particulate Hg (PHg) determination (Lu et al., 1998). After sample collection, the entire sample train trap is sent to a laboratory for analysis. Analysis of the sorbent traps is by CVAFS following strong acid digestion, BrCl oxidation, aqueous SnCl_2 reduction, and dual gold amalgamation (EPA Method 1631B modified). The analysis of the PHg on the flyash is by thermal desorption at 800° C, passing through a heated MnO converter, gold preconcentration and CVAFS detection. In the event of anticipated high flyash loadings, it is recommended for PHg quantification a 47-mm quartz fiber filter should be used for sampling, followed by strong acid digestion and EPA Method 1631 (modified) CVAFS detection.

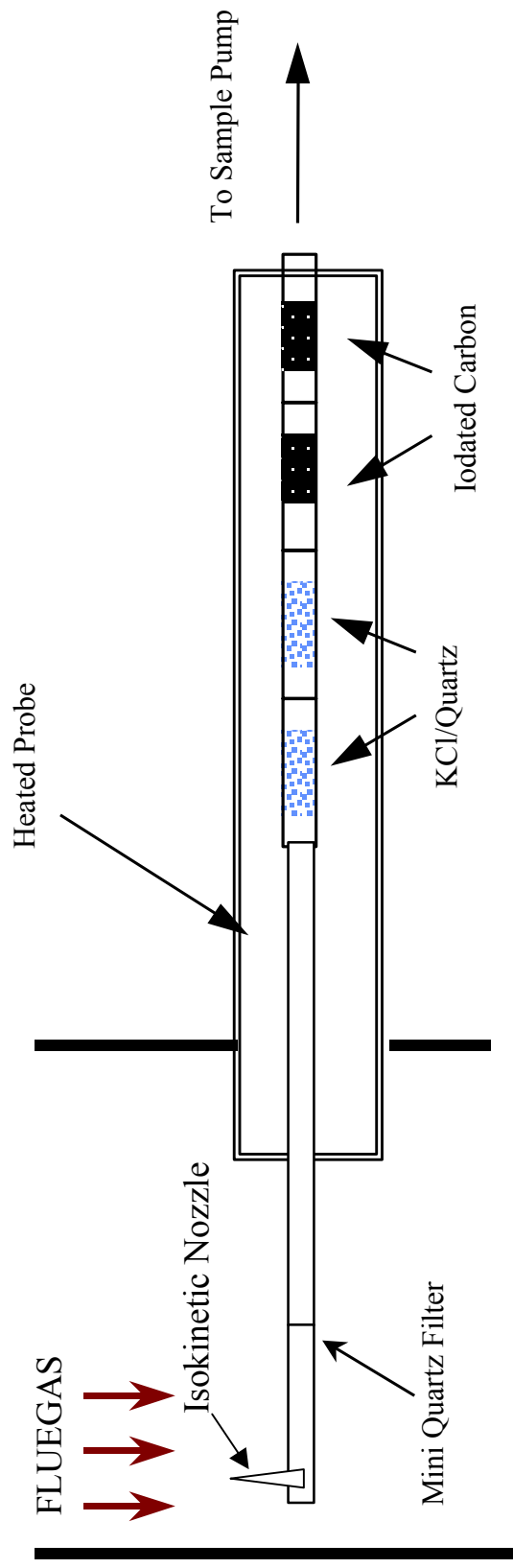


Figure 1. Schematic of the FMSS Solid Sorbent Sample Train

The intent of the PBMS approach for the FMSS method evaluation is to define and determine under real conditions the quality control requirements, matrix suitability and laboratory reproducibility, method detection limit, ruggedness, accuracy, precision, bias, and interference,. All aspects of the PBMS analytical protocol were addressed in this study. The majority of the PBMS study was conducted at the Energy and Environmental Research Center (EERC) Pilot Plant. One important aspect of the PBMS is to collect samples in different fluegas systems, coal type, sampling technicians and analysis technicians. This was accomplished in a similar intercomparison study of the FMSS and OH Method at the US DOE National Energy Technology Laboratory (DOE/NETL-2001/1147 "Comparison of Sampling Methods to Determine Total and Speciated Mercury in Flue Gas," CRADA 00-F038 Final Report). Most importantly, for this study, all FMSS Method sample runs were collected in parallel with the ASTM approved Ontario Hydro (OH) Method. The study was conducted using various fuels, two types of particulate control devices, selective fluegas Hg species spiking and both sample flow rate and temperature variations. For all tests, at least a duplicate FMSS and OH sample were collected, and frequent quadruplicate samples were collected for the FMSS.

The full matrix of 16 tests at the EERC facility are listed below in Table II-1.

Table II-1: Summary of FMS Tests at EERC

Sample Date	Run	Fuel	PCD	Hg Spiked	OH Samples	FMS Samples	Notes
3/6/00	0	Nat'l Gas	Baghouse	none	none	4	MDL-precision at low level [Hg]
3/7/00	0	Nat'l Gas	Baghouse	none	none	5	MDL-precision at low level
3/7/00	1	Nat'l Gas	Baghouse	Hg ⁰	2	3 + FB	Hg ²⁺ Bias Check – clean matrix
3/7/00	2	Nat'l Gas	Baghouse	HgCl ₂	2	3 + FB	Hg ⁰ Bias Check – clean matrix
3/8/00	3	Bit. Coal	ESP	none	2	4	Flow rate variation
3/8/00	4	Bit. Coal	ESP	none	2	8	MDL – precision at mid level [Hg]
3/10/00	5	Bit. Coal	ESP	none	2	2 + FB	Replicates at mid level [Hg]
3/13/00	6	Bit. Coal	ESP	HgCl ₂ + Hg ⁰	2	2	Spike recovery replicates
3/13/00	7	Bit. Coal	ESP	HgCl ₂ + Hg ⁰	2	2 + FB	Spike recovery replicates
3/13/00	8	Bit. Coal	ESP	HgCl ₂ + Hg ⁰	2	2	Spike recovery replicates
3/14/00	9	Bit. Coal	ESP	HgCl ₂ + Hg ⁰	2	3 + FB	Spike recovery replicates
3/14/00	10	Bit. Coal	ESP	HgCl ₂ + Hg ⁰	2	3 + FB	Spike recovery replicates
3/15/00	11	Bit. Coal	Baghouse	none	2	3 + FB	Replicates at mid level [Hg]
3/15/00	12	Bit. Coal	Baghouse	none	2	4	Sorbent temperature variation
3/16/00	13	Bit. Coal	Baghouse	HgCl ₂ + Hg ⁰	2	4	Sorbent temperature variation
3/16/00	14	Bit. Coal	Baghouse	HgCl ₂ + Hg ⁰	2	3 + FB	Spike recovery replicates
3/16/00	15	Bit. Coal	Baghouse	HgCl ₂ + Hg ⁰	2	4	Flow rate variation
3/17/00	16	Bit. Coal	Baghouse	HgCl ₂ + Hg ⁰	2	7	MDL – precision at high level [Hg]
Total					32	66 + 8FB	

II.A Justification

Hg speciation is important both as an aid to engineering efforts focused on Hg control; and as a tool for evaluating the fate and transport of Hg, since fuel combustion is a significant input of anthropogenic Hg to the atmosphere. As each species has dramatically different chemical and biological properties, understanding its speciation directly effects our ability to model its effects (Bullock et al, 1997, Pai et al.1996).

II.B Historical Studies of Interest

Bloom (1993) identified a need to develop and verify methods to accurately quantify the mercury speciation in combustion fluegases. Prestbo and Bloom (1994, 1995) introduced the MESA method, a much simpler and more economical sampling collection method than the complex bubbling systems that were currently employed in stack-gas monitoring. The MESA sampling system for gas phase Hg employed a series of heated, solid phase adsorbent traps. Flue-gas oxidized Hg species (Hg^{+2}) are adsorbed by a potassium chloride (KCl) impregnated soda lime sorbent. Elemental Hg (Hg^0) is collected by an iodated-carbon sorbent after passing through the KCl/lime. The MESA method had several distinct advantages over the impinger methods, namely: lower detection limits, simplified sample collection, and the added value provided by the species information. Although the MESA method was able to measure THg accurately to within $\pm 10\%$ of accepted methods (Nott et al., 1994, Laudal et al., 1997, Prestbo and Bloom, 1995), the major disadvantage of the MESA method was non-quantitative collection of particulate material. (Prestbo and Bloom, 1995) and possible over-estimation of the oxidized fraction at high SO_2 (Laudal, 1997, Chu and Porcella, 1995) compared to the liquid impinger based methods. The major disadvantages of the impinger methods have been discussed in detail elsewhere (Meij, 1991) but are namely the cost, hazardous chemical transport, large sample volume needed to overcome the high Hg blanks, SO_2 interference, and wall losses.

Because the MESA method was mechanically much easier, Frontier Geosciences set out to improve the method by modifying the sorbents. They initiated some internally funded bench scale experiments, and eventually showed that the positive bias of the MESA method Hg^{+2} was not found when sulfur levels were low ($< 500\text{ppm}$) (Prestbo and Tokos, 1997). Also replaced was the first dry sorbent, KCl/lime, with KCl/quartz. This new method has since been referred to as the Fluegas Mercury Sorbent Speciation method or FMSS.

Ongoing tests in the past year of the FMSS method in numerous studies have shown that the potential for bias has been eliminated by this change in solid sorbent chemistry. What follows are experimental results from a rigorous evaluation of the FMSS method, including technical information about the method. By directly comparing the FMSS method to the ASTM standard Ontario Hydro (OH) method, validation of the FMSS method will result with acceptable accuracy, precision for total and speciated mercury.

II.C Objectives

The objectives of this study were twofold. First, was to collect good quality data based on the 'test matrix' presented in Table II-1 and to evaluate the FMSS method under the EPA's new PBMS relative the EPA standard OH method. And second, the object was to define and determine under real conditions the scope, quality control requirements, method detection limit, ruggedness, accuracy, precision, interferences, matrix suitability and laboratory reproducibility.

II.D Target Analytes

In combustion fluegas, mercury is present as elemental (Hg^0), oxidized (or Hg^{+2}) and particulate (PHg) forms. Total Hg (THg) is the sum of the gas phase Hg^0 and Hg^{+2} and PHg. The $\%\text{Hg}^{+2}$ is the fraction of the Hg that exists as Hg^{+2} . The symbols that will be referred to through out the document are listed in Table II-2.

Table II-2

Nomenclature of the Target Analytes

Particulate Hg	PHg
Elemental Hg	Hg^0
Oxidized Hg	Hg^{+2}
Total Hg	$\text{THg} = \text{Hg}^0 + \text{Hg}^{+2} + \text{PHg}$
Percent Oxidized Hg	$\%\text{Hg}^{+2} = \text{Hg}^{+2} / \text{THg}$

II.E Applicable Matrices

The applicable matrices for the FMSS method include fluegas from the combustion of natural gas and/or coal in the presence of SO_2 , NO_x , HCl, and flyash. It is expected that the FMSS method will be applicable to other fluegas matrices, such as from municipal waste incinerators, sewage sludge incinerators, smelting and other high temperature or combustion processes. However, the limitations of this study are for coal fluegas only.

II.F Availability of Equipment

Fluegas is a challenging sampling environment. However, the equipment required to collect the FMSS method samples are standard air sampling equipment, such as in-stack probes, mass flow meters, sampling media or solid sorbents, and temperature controllers (Table II-3). The handling procedures are technical, but easy to learn for an experience stack sampler. The FMSS method sorbents are made routinely at Frontier Geosciences with careful screening to make sure blanks are low and consistent (<1 ng/trap). Hg analysis requires setting up a low-level cold vapor atomic fluorescence spectrometer (CVAFS) system as described in EPA Method 1631 and EPA document "Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities." For shipping, the FMSS traps do not need hazardous or controlled substance designations.

Table II-3
Availability of Equipment

	Requirement	Availability of Equipment
CLEAN HANDLING TECHNIQUES	Standard Clean Handling Field Techniques less than 2 hours of training	Standard Stack Sampling Capabilities
GAS SAMPLING TRAPS AND MEDIA	Mini-particulate filter (Quartz-fiber filter in quartz tube on nickel support screen) for PHg	Standard Procedure at FGS
	KCl/quartz traps for gaseous Hg ⁺²	Standard Procedure at FGS
	Iodinated carbon trap for Hg ⁰	Standard Procedure at FGS
TEMPERATURE CONTROL	Temperature control requirements of 90+/-5 deg C using heated probes and temperature controllers	Standard Procedure at FGS
FLOWRATE CONTROL	Flow Rate control requirements of 0.4 +/- 0.1 slpm with fluegas pulled by vacuum to mass flow meters	Standard Procedure at FGS
ANALYTICAL LABORATORY CAPABILITIES	Mercury determinations by CVAFS	Standard CVAFS Analytical Capabilities
	Sorbent traps analyzed by strong acid digestion, BrCl oxidation, aqueous SnCl ₂ reduction, and dual gold amalgamation.	EPA Method 1631B Modified
	Analysis of PHg by thermal desorption at 800 deg C, with MnO converter, gold preconcentration and CVAFS detection	EPA Method 1631B Modified

II.G Cost of Hg Speciation Methods

The costs to perform the FMSS method should be most comparable to the Ontario Hydro method based on most similar inlet configurations and principles of operation. Continuous emission measurement or CEM methods although operating are included here for comparison of costs basis, but the meaning is less valuable, since it operates on different inlets and operating principles. The costs to perform Hg Speciation Methods are outlined in Table II-4. Because it is simple to operate, it requires only a few man-hours to learn.

Table II-4

Cost of Hg Speciation Methods

Hg Speciation Method	Sampling Method	Analytical Method	Approximate Cost for a 3-Day Field Sampling Campaign and Laboratory Analysis
FMSS	Non-continuous	CVAFS	\$10,000
Ontario Hydro	Non-continuous	CVAA	\$30,000
Continuous Emission Monitor	Continuous	CVAFS or CVAA	\$30,000

III. QUALITY CONTROL REQUIREMENTS (Method Quality Objectives)

Presented here is the quality control defined and determined under real conditions for experiments at the EERC. This provided the ongoing quality assurance performance evaluations required by the PBMS, and defines ongoing future evaluations. The numerous results include replicate analysis, laboratory and field blanks, recoveries of standard reference materials, recoveries of matrix spikes, temperature and volume control requirements. Based on the performance of the FMSS method under real conditions during these tests, method quality objectives (MQO) were set. Although the specific results of the study are better than the following MQOs, the MQOs are set higher so that future applications of the method by new users could reasonably be achieved.

III.A Replicate Analysis

This section discusses the replicate analysis in the laboratory and provided the means to measure the precision of the CVAFS analytical method. In most cases, laboratory replicate analysis occurred on the same analysis day, using the same instrument. However, in some instances, replicates sample analysis occurred on different days and in some cases using different instruments. For samples analyzed in duplicate (n=2), a relative percent difference (RPD) was calculated as a percentage using the formula:

$$RPD = \frac{ABS[A-B]}{AVG(A+B)}$$

Laboratory replicate results are presented as analytical duplicates in Table III-1.

Table III-1
FMSS Replicate Analysis

A. ANALYTICAL DUPLICATES for PHg				
Particulate Hg	Rep 1	Rep 2	mean	RPD or RSD
PHG-6-031400	139.9	146.8	143.3	4.8%
PHG-6-031300	23.1	22.79	23.0	1.6%
PHG-5-031400	129.7	147.8	138.8	13.0%
PHG-4-030800	11.5	13.8	12.6	18.5%
PHG-3-031400	91.0	100.9	95.9	10.3%
PHG-2-031400	61.9	64.0	63.0	3.3%
PHG-2-030800	11.5	11.0	11.3	4.5%
PHG-1-031300	15.3	14.82	15.1	3.5%
PHG-2031400	60.6	63.3	61.9	4.5%
			MEAN	7.1%
			STDEV	5.6%
B. ANALYTICAL DUPLICATES (KCLA and KCLB) for Hg ⁺²				
	Rep 1	Rep 2	mean	RPD or RSD
KCLA-9-030800	161.96	181.3	171.6	11.2%
KCLA-8-031500	241.8	258.3	250.1	6.6%
KCLA-7-031700	838.9	824.1	831.5	1.8%
KCLA-7-031600	577.3	621.74	599.5	7.4%
KCLA-7-031500	221.5	209.0	215.3	5.8%
KCLA-7-031400	191.9	352.9	272.4	59.1%
KCLA-7-031300	522.11	522.10	522.1	0.00%
KCLA-6-031700	1003.1	840.6	921.9	17.6%
KCLA-6-031500	246.5	240.7	243.6	2.4%
KCLA-6-031400	128.2	208.2	168.2	47.5%
KCLA-6-031300	692.5	619.3	655.9	11.2%
KCLA-5-031400	406.8	434.5	420.7	6.6%
KCLA-4-031600	621.7	678.6	650.1	8.8%
KCLA-4-031300	766.9	644.54	705.7	17.3%
KCLA-4-030800	166.5	199.2	182.8	17.9%
KCLA-3-031700	882.7	735.7	809.2	18.2%
KCLA-3-031600	812.6	651.8	732.2	22.0%
KCLA-3-031400	628.4	565.0	596.7	10.6%
KCLA-3-031300	589.0	670.56	629.8	13.0%
KCLA-3-030800	234.2	203.8	219.0	13.9%
KCLA-2-031700	869.6	730.9	800.2	17.3%
KCLA-2-031600	761.6	711.1	736.4	6.9%
KCLA-2-031600	660.6	761.6	711.1	14.2%
KCLA-2-031400	556.5	451.0	503.8	20.9%
KCLA-1-031700	905.70	736.0	820.9	20.7%
KCLA-1-031600	742.3	895.7	819.0	18.7%
KCLA-1-031600	895.7	742.3	819.0	18.7%
KCLA-1-031400	482.9	414.9	448.9	15.1%
KCLA-10-030800	133.86	152.1	143.00	12.8%
KCLB-7-031300	150.3	153.4	151.8	2.0%
KCLA-10-030700	378.9	384.6	381.7	1.5%
KCLA-2-030800	177.0	180.7	178.9	2.1%
			MEAN	14.1%
			STDEV	12.3%

Table III-1 (continued)

C. ANALYTICAL DUPLICATES (ICA) for Hg ⁰				
	Rep 1	Rep 2	mean	RPD or RSD
ICA-9-030800	7.46	7.74	7.60	3.7%
ICA-7-031700	196.8	186.3	191.6	5.5%
ICA-7-031600	238.6	215.67	227.2	10.1%
ICA-7-031400	18.8	14.2	16.5	27.8%
ICA-7-031300	191.1	171.71	181.4	10.7%
ICA-6-031700	249.1	220.0	234.6	12.4%
ICA-6-031400	10.4	7.28	8.9	35.6%
ICA-5-031400	22.4	18.81	20.6	17.3%
ICA-4-031600	231.2	202.3	216.7	13.3%
ICA-4-030800	16.3	19.61	17.9	18.8%
ICA-3-031700	234.2	194.5	214.3	18.5%
ICA-3-031600	171.5	169.8	170.6	1.0%
ICA-3-031400	15.4	17.01	16.2	9.7%
ICA-3-030800	17.4	15.75	16.6	9.8%
ICA-2-031700	253.6	220.4	237.0	14.0%
ICA-2-031600	214.7	220.0	217.3	2.4%
ICA-2-031600	225.2	214.7	220.0	4.8%
ICA-2-031400	14.4	11.28	12.8	24.3%
ICA-2-031000	8.3	6.79	7.57	20.6%
ICA-2-030800	13.2	10.9	12.0	19.2%
ICA-1-031700	256.54	233.4	245.0	9.5%
ICA-1-031600	194.0	237.1	215.6	20.0%
ICA-1-031600	237.1	194.0	215.6	20.0%
ICA-1-031400	14.1	11.3	12.7	21.8%
ICA-1-031000	17.4	4.63	11.00	115.8%
ICA-10-030800	4.69	5.2	4.92	9.4%
ICA-7-030700	389.2	395.0	392.1	1.5%
ICA-11-030800	47.8	48.4	48.1	1.4%
			MEAN	17.1%
			STDEV	21.2%

The mean precision of the laboratory replicates was 7.1% for PHg, 17.1% for Hg⁰, and 14.1% for Hg⁺². Based on this result, the MQO for future studies was estimated to be 25% for laboratory replicates.

III.B Field Blanks

Field blanks provided the overall blank, including sample handling in the field, transportation, storage and handling, analytical and matrix considerations. Field blanks were identical to field samples except that the field blanks were downloaded in the field without sampling. Eight field blanks were collected for each type of the sample traps. The means and standard deviations of the means for the field blanks are shown in Table III-2.

Table III-2

FMSS Field Blank Summary

FIELD BLANKS						Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result			
RESULT	PHg	KCLA	KCLB	ICA	T-Vol	[pHg]	[Hg ⁰]	[Hg ⁺²]	[THg]
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter	ug/m ³	ug/m ³	ug/m ³	ug/m ³
FMS-9-030700 FB	nc	0.1473	0.0859	0.145	30.0	na	0.0048	0.0078	0.0126
FMS-13-030700 FB	nc	2.78	0.0205	0.015	30.0	na	0.0154	0.0029	0.0183
FMS-3-031000 FB	0.0419	0.0395	0.0000	0.490	30.0	0.0014	0.0163	0.0013	0.0177
FMS-5-031300 FB	na	0.3990	0.0000	0.377	30.0	na	0.0126	0.0000	0.0126
FMS-4-031400 FB	0.0239	0.0000	0.0000	0.416	30.0	0.0008	0.0139	0.0000	0.0139
FMS-8-031400 FB	0.132	0.0356	0.0823	0.371	30.0	0.0044	0.0124	0.0039	0.0163
FMS-4-031500 FB	nc	0.0000	0.0000	0.640	30.0	na	0.0213	0.0000	0.0213
FMS-8-031600 FB	nc	0.2026	0.0000	0.789	30.0	na	0.0263	0.0068	0.0330
2.78 t-test									
n=8						FMSS mean	0.0022	0.0154	0.0028
						STDEV	0.0019	0.0064	0.0031
One KCLA value was removed by t-test and replaced by mean.						MDL-A	0.0058	0.0192	0.0093
							0.0202		

Hg trap concentrations (on the left) were used to determine fluegas concentrations (on the right) based on the mean sample volume of 30.0 standard liters. Hg⁺² was determined by KCLA + KCLB; Hg⁰ was determined by ICA ng/trap values. In one case, the KCLA value was considered bad and the value was thrown out based on the result of a t-test.

Laboratory blanks were analyzed along with the calibration curve and then at a rate of 1-in-10 samples thereafter. Based on standard operating procedures of the analytical laboratory laboratory blanks were always less than 1 ng and are available if requested for review.

The method quality objectives or MQOs for field blanks in future studies were estimated based on the results at the EERC and are shown in Table III-3

Table III-3

Field Blank Method Quality Objectives

Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result				
MQO FOR FIELD BLANKS	PHg ug/m ³	Hg ⁰ ug/m ³	Hg ⁺² ug/m ³	THg ug/m ³
LESS THAN	0.02	0.05	0.05	0.05
(STDEV) +/-	0.01	0.02	0.02	0.02

III.C Standard Reference Materials

Standard Reference Material (SRM) spikes and recoveries were used to provide ongoing evaluation of the accuracy of the overall analytical method. The SRM was spiked to a CVAFS analytical bubbler and the recovery of the SRM was calculated in percent as the measured divided by the expected concentration. The SRM used during this study was NIST 1641d, which was standardized by the National Institute of Science & Technology for total Hg. The SRM was analyzed a minimum of once per analysis day and typically several times throughout the day. SRM recovery data are reported in Table III-4.

Table III-4
SRM Recoveries

SRM Recovery of NIST 1641d		
Analysis Date	ng/aliquot	% Recovery
3/16/00	1.583	99.6%
3/16/00	1.336	84.0%
4/27/00	1.731	111.1%
4/27/00	1.661	106.6%
4/28/00	1.618	103.8%
4/28/00	1.527	98.0%
5/1/00	1.456	93.4%
5/1/00	1.491	95.6%
	MEAN	99.0%
	STDEV	8.4%

SRM recoveries averaged $99.0 \pm 8.4\%$ and were considered good. The MQOs for future studies were estimated based on this result. The MQO for SRM Recoveries of $100 \pm 20\%$ would be easily obtainable in future studies.

III.D Matrix Spike Recoveries

Matrix spike recoveries provided an ongoing evaluation of the accuracy of the analytical method for Hg^0 and Hg^{+2} in the presence of the sampling matrix. Matrix spike recoveries were calculated for 1.00ng additions to laboratory analytical bubblers, which contained a sample aliquot.

Recoveries of the 1.00ng matrix spikes are shown in Table III-5. The percent recovery was calculated as:

$$\% \text{ Recovery} = (\text{ng/aliquot of sample with spike}) / (\text{ng/aliquot of sample} + 1.00 \text{ ng})$$

Table III-5
Matrix Spike Recoveries

1.00 ng Analytical Matrix Spikes	
Sample ID	% Recovery
ICA-SOH-7-0307 AS + 1.0 ng	98.0%
KCLA-SOH-10-0307 AS + 1.0 ng	92.8%
KCLA-2030800 AS + 1ng	106.4%
IC-A-11030800 AS + 1ng	107.7%
KCLB-7031300 AS + 1ng	105.0%
PHG-2031400 AS + 1ng	95.5%
KCLA-5031500 AS + 1.0 ng	100.7%
MEAN	100.9%
STDEV	5.72%

Matrix spikes averaged $100.9\% \pm 5.7\%$ and were similar for the different types of samples. The MQO for matrix spikes for future studies was estimated based on these results for Lab Analysis Spike Recoveries to be $100 \pm 20\%$.

III.E Temperature Control

Probe temperatures during normal application of the FMSS method at the EERC were held constant at $90 \pm 5^\circ\text{C}$ using heated-probes and Omega temperature controllers. This is the ideal working temperature range and indicates a relative percent difference of 6%. Proper temperature control during normal application at the EERC was almost always successful, except in a few cases in when condensation was noted on the sample traps upon downloading, which indicated a problem or failure of temperature control. In these cases the sample was compromised and it was noted in the sampling logs.

The importance of the sampling probe temperature to Hg determination was investigated during two quadruplicate temperature tests (Runs 12 and 13). During these runs, four parallel samples were collected that were identical except that probe temperature was varied from 75 to 105°C . This represented a range in temperatures that is one to three times the ideal FMSS range. Temperature control and data for the temperature test results are summarized in Table III-6.

Several points will help in the interpretation of Table III-6. The precision of the temperature control is given as an RSD at the top of the table (A). The analytical data during ruggedness tests is presented at the bottom of the table (B). T-Vol (column 3) is the temperature corrected dry gas volume. Breakthrough is calculated as KCLB/KCLA (column 6). In ideal situations, the breakthrough to the KCLB trap is low ($<2\%$), and even this is taken into consideration by the method as the Hg concentrations on both traps are used to determine Hg^{+2} concentrations. For these tests breakthrough was used to indicate the collection efficiency of the KCl traps for Hg^{+2} during ruggedness tests.

Table III-6

A. Temperature Control at the EERC

OVERALL TEMPERATURE CONTROL AT EERC	
	PROBE TEMP %RSD
Ruggedness , FR Tests	< 6%
Ruggedness , Temp Tests	14.2%
ESP malfunction, additional ruggedness	< 6%
Natural Gas No Tests	< 6%
Bitcoal No Tests	< 6%

B. Temperature and Breakthrough during ruggedness tests

RUN 12 ANALYTICAL TRAP DATA

	Temp	KCLA	KCLB	ICA	T-Vol	$KCLB/KCLA$
	C	ng/trap	ng/trap	ng/trap	corr., liter	%
FMS-5-031500	75.7	217.7	0.09	3.03	26.0	0.04%
FMS-6-031500	88.4	243.6	0.04	5.88	26.2	0.01%
FMS-7-031500	96.4	215.3	0.19	3.09	26.3	0.09%
FMS-8-031500	105.7	250.1	0.35	4.54	26.4	0.14%
mean	91.6					
T, RSD	13.91%					

RUN 13 ANALYTICAL TRAP DATA

Run 15	Temp	KCLA	KCLB	ICA	T-Vol	$KCLB/KCLA$
	C	ng/trap	ng/trap	ng/trap	corr., liter	%
FMS-1-031600	75.3	819.0	15.3	215.6	26.5	1.87%
FMS-2-031600	86.7	711.1	14.9	220.0	26.4	2.10%
FMS-3-031600	96.6	732.2	6.9	170.6	26.3	0.94%
FMS-4-031600	105.9	650.1	61.3	216.7	26.4	9.43%
mean	91.1					
T, RSD	14.45%					

The results of the ruggedness temperature tests are presented elsewhere (see section IV). However, no significant trends were observed between Hg concentration and probe temperature, even at the highest temperature when the breakthrough from the KCLA trap to KCLB trap was significantly higher than the other traps (see $KCLB/KCLA$ in Table III-6). However, the highest temperature (~106°C) was almost four times above the control range and despite the breakthrough, the precision and accuracy were still good.

III.F Flow Rate Control

The ideal flowrate is nominally 0.4 ± 0.1 slpm so that the nozzle diameter must be chosen based on flue gas flow rates to maintain isokinetic sampling conditions within $\pm 25\%$ (see section III-H). At EERC, the ideal flowrate range was 0.4 ± 0.1 slpm. Flow rate control was obtained using flow control valves and mass flow meters (Sierra). Flow rates were recorded manually at the beginning and end of the sample, and most often at quarter points in between. Flow rates were used to determine sample volume based on sample collection times, and a correction to dry gas volume was made based on temperature. Volumes are reported at standard temperature (20°C) and pressure (1 atmosphere) in standard liters per minute (slpm). At the EERC all samples were in the ideal flowrate range (unless indicated in the sample logs) and generally flowrate varied by less than 3% (See RSD, Table III-5). Normal flowrate control was not maintained during Runs 9 and 10 when the ESP was malfunctioning and PHg loading was extremely high, which provided an unexpected ruggedness test.

The importance of flowrate to Hg determinations was evaluated during two quadruplicate flowrate tests during Runs 3 and 15. During these runs four parallel samples were collected that were identical except the collection flow rates was varied from 0.25 to 0.85 slpm. This represented flow rates that were two to four times the ideal FMSS range. Flowrate control and the analytical data for the flowrate ruggedness tests are summarized in Table III-7.

Several points will help in the interpretation of Table III-7. The precision of the flowrate control at the EERC is given as RSD at the top (section A). The analytical data during ruggedness tests is presented at the bottom (section B). T-Vol (column 3) is the temperature corrected dry gas volume and breakthrough is calculated as KCLB/KCLA (column 6).

Table III-7

A. Flowrate Control at the EERC

OVERALL FLOWRATE CONTROL AT EERC	
	COLLECTION FLOW RATE
	%RSD
Ruggedness , FR Tests	41.3%
Ruggedness , Temp Tests	0.6%
ESP malfunction, additional ruggedness	26.1%
Natural Gas No Tests	9.3%
Bitcoal No Tests	2.8%

Table III-7 (continued)
B. Flowrate and breakthrough during ruggedness tests

RUN 3 ANALYTICAL TRAP DATA

Run 3*	Flow Rate	PHg	KCLA	KCLB	ICA	T-Vol	$KCLB/KCLA$
	slpm	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter	%
FMSS-1-030800**	0.22	na	88.81	0.35	5.79	9.1	0.4%
FMSS-2-030800	0.44	11.15	178.9	1.366	12.04	23.6	0.8%
FMSS-4-030800***	0.44	na	234.2	0.776	16.56	35.1	0.3%
FMSS-3-030800	0.57	13.81	199.2	0.347	19.61	24.4	0.2%
mean	0.42	* heavy particulate noted all samples					
FR, %RSD	33.9%	** condensation noted					
		***failure to maintain 0.8 slpm, rapid drop in flowrate					

RUN 15 ANALYTICAL TRAP DATA

Run 15	Flow Rate	PHg	KCLA	KCLB	ICA	T-Vol	$KCLB/KCLA$
	slpm	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter	%
FMSS-9-031600	0.24	nc	467.1	7.10	123.7	14.6	1.5%
FMSS-10-031600	0.47	nc	836.7	7.67	193.9	26.3	0.9%
FMSS-11-031600	0.60	nc	1060	12.5	362.5	38.0	1.2%
FMSS-12-031600	0.88	nc	1353	132.7	534.8	50.8	9.8%
mean	0.55						
FR, %RSD	48.8%						

The results of the quad flowrate tests are reported elsewhere (see section VI). However, no significant trends were observed between Hg concentration and flowrate, even at the highest flowrate where the breakthrough from the KCLA trap to KCLB trap was greatest (See KCLB/KCLA in Table III-7). However, this flowrate is almost five times above the control range and despite the breakthrough, the precision and accuracy was still good.

III.G Isokinetic sampling tolerance limits

In order to keep it simple, the FMSS method is designed to be only semi-isokinetic. Thus, the inlet nozzle diameter is chosen to match the flue gas flow rate and the FMSS method flow rate range of 0.4 ± 0.1 slpm. During sampling, there is no adjustment for changing flue gas flow. This approach works because most coal flue gas has less than 5% PHg and the Hg is associated with sub-micron particles that will sample like a gas. Thus the MQO for semi-isokinetic sampling is $\pm 50\%$. If however there is reason to sample within a $\pm 10\%$ tolerance for isokinetics, this is certainly possible using standard EPA isokinetic stack sampling methods.

III.H Summary of Method Quality Objectives

Method quality objectives or MQOs were defined based on the performance of the FMSS method during the quality control experiments for the EERC and are summarized here.

Table III-8

A. MQOs for the quality control of future studies

	IDEAL FMSS Method	FMSS Method Result EERC	FMSS Method Future Studies MQO
Laboratory Replicate	$\pm 25\% \text{RPD}$	$< 20\% \text{RPD}$	$\pm 25\%$
SRM Spike Recoveries	$100 \pm 20\%$	$99 \pm 8\%$	$100 \pm 20\%$
Matrix Spike Recoveries	$100 \pm 20\%$	$100.9 \pm 5.7\%$	$100 \pm 20\%$
Temperature Control	$90 \pm 5^\circ \text{C}$ or $6\% \text{RPD}$	$90 \pm 5^\circ \text{C}$ or $6\% \text{RPD}$	$90 \pm 5^\circ \text{C}$ or $6\% \text{RPD}$
Flow Rate Control	$0.4 \pm 0.1 \text{slpm}$ or $25\% \text{RPD}$	$0.4 \pm 0.05 \text{slpm}$ or $2.1\% \text{RPD}$	$0.4 \pm 0.1 \text{slpm}$ or $25\% \text{RPD}$

Several points may help in the interpretation of Table III-8. The numerous quality control experiments are listed in column 1. The Ideal Result (column 2) is the performance level required to satisfy the current needs of the Hg fluegas sampling community. This need was estimated as 5 ug/m^3 levels of Hg in fluegas with a precision or RSD of $\pm 20\%$ (or $0.5 \pm 0.1 \text{ ug/m}^3$ at $n=3$) and of better than 90% for THg and $\% \text{Hg}^{+2}$. The FMSS Method performance result at the EERC is listed in column 3 and the MQO for future studies as it applies to Hg speciation in combustion fluegas matrices is listed in column 4.

IV. FMSS Method Detection Limits

Method detection limits or MDLs were estimated in three ways and were based on the analysis of A) Eight field blanks; B) Eight samples collected at near blank levels (Run 0) and C) Eight Low-level, Mid-level, and High level samples.

MDL estimates by each method are discussed below and were based on the data in Table IV-1.

Table IV-1

Data for FMSS MDL estimates

A. MDL DATA AT THE EERC							
Analysis of Eight Each of	MDL method			Mean PHg ug/m ³	Mean Hg ⁰ ug/m ³	Mean Hg ⁺² ug/m ³	Mean THg ug/m ³
MEAN							
EERC Field Blanks	A		mean	0.0022	0.0154	0.0028	0.0182
EERC Run 0	B,C	Low level	mean	NA	0.0215	0.0063	0.0277
EERC Run 4	C	mid level	mean	0.0070	0.303	8.36	8.66
EERC Run 16	C	high level	mean	NA	8.74	33.1	41.8
STDEV							
EERC Field Blanks	A	n=8	stdev	0.0019	0.006	0.003	0.007
EERC Run 0	B,C	n=8	stdev	NA	0.011	0.009	0.017
EERC Run 4	C	n=6	stdev	0.005	0.087	0.67	0.68
EERC Run 16	C	n=8	stdev	NA	1.02	1.86	2.69
B. MDL C - GRAPH DATA							
MDL-C CALCULATION				MDL PHg ug/m ³	MDL Hg ⁰ ug/m ³	MDL Hg ⁺² ug/m ³	MDL THg ug/m ³
FMSS GRAPH DATA:							
Mean(x-axis) vs Stdev(y-axis)	C	slope		NA	0.1138	0.0541	0.0361
Mean(x-axis) vs Stdev(y-axis)	C	y-int		NA	0.0301	0.0969	0.0688
Mean(x-axis) vs Stdev(y-axis)	C	R ²		NA	0.9984	0.9871	0.9980

Method A MDLs were generated based on 3 σ of the field blanks (see Table III-2).

Method B MDLs were generated based on 3 σ of Run 0. Run 0 was burning natural gas with SO₂ and HCl without Hg spiking.

Method C MDLs were generated based on the MDL plots of mean Hg concentrations (x-axis) verses standard deviation of the means (y-axis) for the low level, mid-level and high-level replicate of Run 0, 4 and 16. The MDL plots for method C are shown in Figure IV-1.

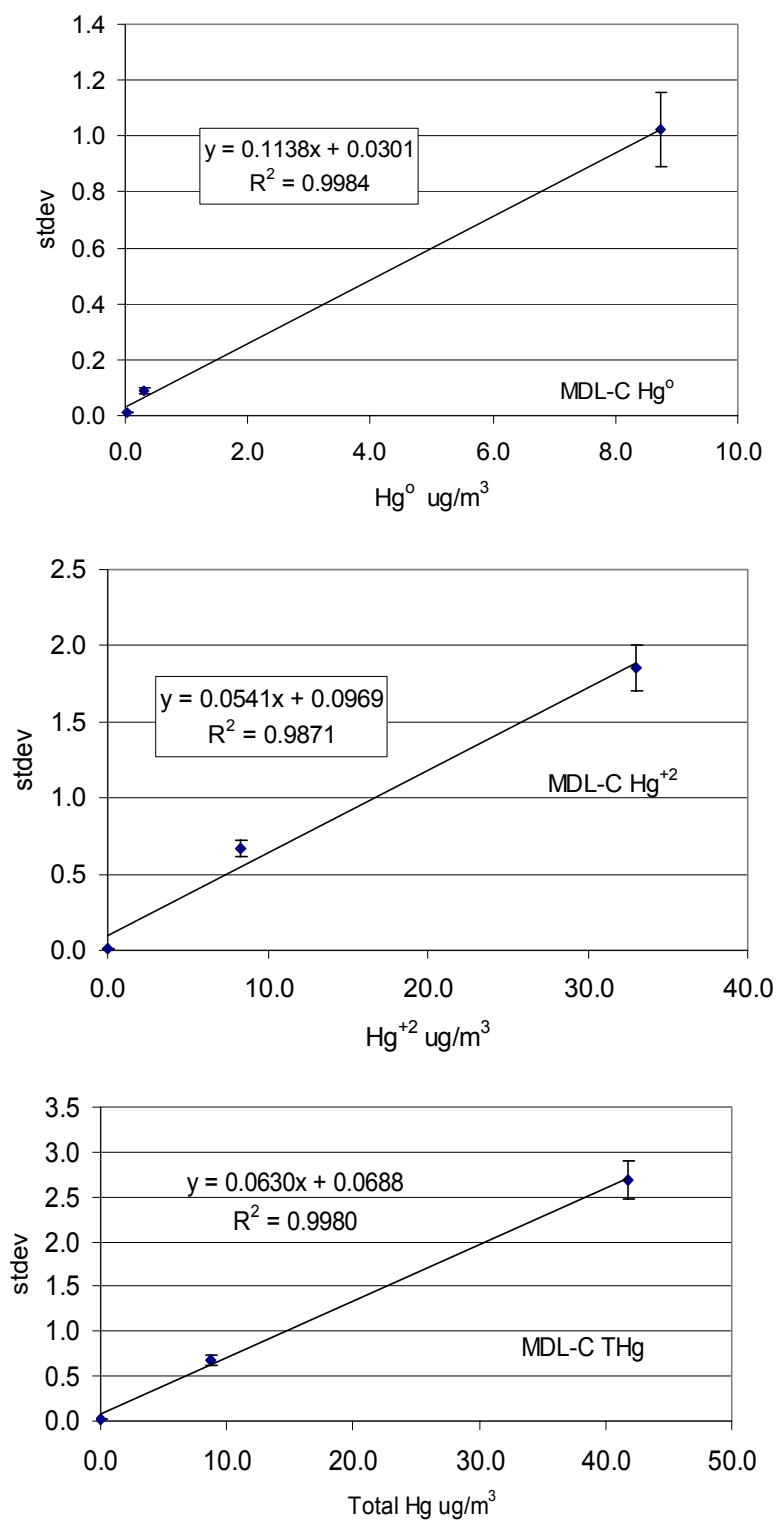


Figure IV-1

Hg concentration versus standard deviation for Runs 0, 4 and 16 at the EERC

MDL estimates are summarized in Table IV-2.

Table IV-2

Summary of the FMSS MDL estimates at the EERC

FMSS MDL ESTIMATES RESULT SUMMARY AT THE EERC	FMSS MDL PHg ug/m ³	FMSS MDL Hg ⁰ ug/m ³	FMSS MDL Hg ⁺² ug/m ³	FMSS MDL THg ug/m ³
MDL-A	0.0058	0.019	0.009	0.020
MDL-B	NA	0.032	0.027	0.051
MDL-C	NA	0.090	0.291	0.206
lowest estimate	0.006	0.019	0.009	0.020
highest estimate	0.006	0.090	0.291	0.206
FMSS MDL ESTIMATE*	0.006	0.026	0.018	0.035

* The best MDL estimate was based on the MDL-A and MDL-B result

There was good agreement between the MDL estimated by method A and B. However, MDL estimates by method C were three to ten times higher¹. Based on the higher uncertainties associated with this method, the best estimate for the FMSS MDL was determined by the mean of method A and method B (see Table IV-2).

In conclusion, FMSS MDL estimates at the EERC were (in ug/m³) 0.006 for PHg, 0.026 for Hg⁰, 0.018 for Hg⁺², and 0.035 for THg. Based on this result, the MQO of future studies (in ug/m³) was defined as 0.01 for PHg, 0.03 for Hg⁰, 0.02 for Hg⁺² and 0.04 for THg.

¹ It should be noted that even the higher MDL estimates of method C (See Table IV-1) are quite good and adequate for understanding the apportionment of Hg in fluegas.

V. Precision, Accuracy, and Bias

The precision accuracy and bias of the FMSS method for the full matrix of 16 tests at the EERC facility are presented in this section. The combustion flue gases measured during these runs were burning various fuels, had two types of particulate control devices, and were selectively spiked with Hg. The precision, accuracy and bias of the replicates with no ruggedness testing are discussed in detail here. The result from the ruggedness tests is included in the tables and the figures presented here, but are discussed later (see ruggedness tests, see Section VI).

V.A Precision

Replicate samples at the EERC provided the means to measure the precision of the FMSS method under real conditions. FMSS and OH precision was calculated for each run using the following formulas. For duplicate samples ($n=2$), a relative percent difference (RPD) was calculated from the absolute difference of the means (as a percentage) from:

$$RPD = \left| \text{Run 1}_{\text{FMSS}} - \text{Run 2}_{\text{FMSS}} \right| / \text{average run 1 \& 2}_{\text{FMSS}}$$

For replicate samples where $n > 2$ then a relative standard deviation (RSD) was calculated from the mean and standard deviation of the mean as a percentage as:

$$RSD = \text{STDEV} / \text{MEAN}$$

The accuracy of the FMSS result is reported relative to the OH method and expressed as a percent recovery of the means of the FMSS and OH methods as

$$\% \text{Recovery} = \text{mean}_{\text{FMSS}} / \text{mean}_{\text{OH}}$$

The mean Hg concentrations and precision of the replicates are presented in Table V-1.

A key for the fluegas conditions or ruggedness test and number of replicates (n) averaged for each run is shown below.

Several points may help in the interpretation of Tables V-1 and V-2. Hg concentrations, precision and accuracy are listed by species in Table V-1. FMSS and OH precision summaries are listed by the EERC run # in Table V-2. Hg concentrations were the means of a number of replicates. FMSS replicates were at least duplicates, and frequently quadruplicates, while OH method replicates were always duplicates except during Runs 1 and 2, when n was one and no precision or accuracy is reported for these runs.

Table V-1
CONDITIONS AT THE EERC

CONDITIONS AT THE EERC			TESTS	number of replicates	fraction as vapor
Date-Starttime					
MDL CALCUALTIONS					
EERC Field Blanks		Field Blanks		n=8	
EERC Run 0	3/6/00-3/7/00	Natural Gas no spikes		n=8	
EERC Run 4	3/8/2000-18:37	Bitcoal ESP with spikes	Quads No Test	n=6	0.98
EERC Run 16	3/17/2000-10:06	Bitcoal BH with spikes	Quads No Test	n=8	1.00
				mean	0.99
				stdev	0.01
QUAD RUGGEDNESS TESTS					
EERC Run 3*	3/8/2000-11:37	Bit-coal ESP no spikes	Flowrate Test	n=4	0.89
EERC Run 12*	3/15/2000-13:55	Bitcoal BH no spikes	Temperature Test	n=4	1.00
EERC Run 13*	3/16/2000-9:23	Bitcoal BH with spikes	Temperature Test	n=4	1.00
EERC Run 15*	3/16/2000-16:13	Bitcoal - BH with spikes	Flowrate Test	n=4	1.00
				mean	0.97
				stdev	0.06
REPLICATES NATURAL GAS					
EERC Run 1	3/7/2000-13:35	Natural Gas	Hg ⁰ spikes	n=3	1.00
EERC Run 2	3/7/2000-16:40	Natural Gas	Hg ⁺² spikes	n=3	0.86
				mean	0.93
				stdev	0.09
REPLICATES COAL FLUEGAS MATRICES					
EERC Run 5	3/10/2000-16:24	Bitcoal ESP no spikes		n=2	0.97
EERC Run 6	3/13/2000-9:20	Bitcoal ESP with spikes		n=2	0.98
EERC Run 7	3/13/2000-14:50	Bitcoal ESP with spikes		n=2	0.99
EERC Run 8	3/13/2000-18:53	Bitcoal ESP with spikes		n=2	0.98
EERC Run 9**	3/14/2000-10:30	Bitcoal ESP with spikes	Heavy Particulate	n=3	0.93
EERC Run 10**	3/14/2000-16:00	Bitcoal ESP with spikes	Heavy Particulate	n=3	0.70
EERC Run 11	3/15/2000-9:40	Bitcoal BH no spikes		n=3	1.00
EERC Run 14	3/16/2000-12:31	Bitcoal BH with spikes		n=3	1.00
				mean	0.87
			*Ruggedness	stdev	0.26
**ESP malfunction, additional ruggedness					

Table V-1

RESULTS BY SPECIES

A. Particulate Hg at EERC

PHg RESULT	number (n)	FMSS Mean PHg	FMSS Precision PHg	Accuracy PHg	OH Mean PHg	OH Precision PHg
ID	replicates	ug/m ³	RSD or RPD	%Rec	ug/m ³	RPD
R4	n=6	0.007	71.3%	NA	0.255	35.29%
R16	n=8	NA	NA	NA	0.025	40.00%
R3*	n=4	0.516	12.8%	30.4%	1.700	NA
R12*	n=4	NA	NA	NA	0.010	0.00%
R13*	n=4	NA	NA	NA	0.020	0.00%
R15*	n=4	NA	NA	NA	0.040	50.00%
R1	n=3	NA	NA	NA	0.020	NA
R2	n=3	NA	NA	NA	1.940	NA
R5	n=2	0.079	53.5%	20.6%	0.385	7.79%
R6	n=2	0.599	NA	105.1%	0.570	31.6%
R7	n=2	0.104	41.0%	34.6%	0.300	6.67%
R8	n=2	0.914	NA	145.0%	0.630	9.52%
R9*	n=3	3.721	31.6%	91.9%	4.05	140%
R10*	n=3	8.140	38.4%	91.6%	8.89	30.6%
R11	n=3	NA	NA	NA	0.040	100%
R14	n=3	NA	NA	NA	0.020	NA

B. Elemental Hg at the EERC

Hg ⁰ RESULT	number (n)	FMSS Mean Hg ⁰	FMSS Precision Hg ⁰	Accuracy Hg ⁰	OH Mean Hg ⁰	OH Precision Hg ⁰
ID	replicates	ug/m ³	RSD or RPD	%Rec	ug/m ³	RPD
R4	n=6	0.303	28.8%	65.2%	0.465	6.45%
R16	n=8	8.74	11.7%	98.1%	8.910	28.5%
R3*	n=4	0.579	31.3%	108.3%	0.535	9.35%
R12*	n=4	0.142	36.3%	39.6%	0.360	5.56%
R13*	n=4	7.78	11.2%	92.0%	8.45	5.21%
R15*	n=4	8.96	15.2%	95.5%	9.38	22.0%
R1	n=3	12.82	3.4%	NA	10.1	NA
R2	n=3	2.10	14.2%	NA	2.11	NA
R5	n=2	0.347	36.4%	75.4%	0.460	0.00%
R6	n=2	4.14	31.6%	70.8%	5.85	40.2%
R7	n=2	7.15	14.3%	105.0%	6.81	4.85%
R8	n=2	5.32	NA	69.9%	7.61	1.31%
R9*	n=3	0.618	18.5%	56.9%	1.09	32.3%
R10*	n=3	0.813	17.5%	47.4%	1.72	15.7%
R11	n=3	0.080	17.1%	18.3%	0.435	16.1%
R14	n=3	9.81	10.5%	107.6%	9.120	12.7%

A. Hg⁺² at the EERC

Hg ⁺² RESULT		FMSS Mean Hg ⁺² ug/m ³	FMSS Precision Hg ⁺² RSD or RPD	Accuracy Hg ⁺² %Rec	OH Mean Hg ⁺² ug/m ³	OH Precision Hg ⁺² RPD
ID	number (n) replicates					
R4	n=6	8.36	7.98%	106.0%	7.88	9.90%
R16	n=8	33.1	5.61%	87.7%	37.7	5.94%
R3*	n=4	7.49	9.93%	86.4%	8.68	7.03%
R12*	n=4	8.84	7.35%	87.8%	10.1	8.74%
R13*	n=4	28.5	7.02%	89.5%	31.85	11.7%
R15*	n=4	30.5	6.86%	103%	29.56	14.1%
R1	n=3	0.023	70.15%	NA	0.230	NA
R2	n=3	14.14	2.65%	NA	6.380	NA
R5	n=2	7.86	9.09%	115.4%	6.81	5.29%
R6	n=2	32.5	1.27%	116.1%	28.0	17.5%
R7	n=2	26.3	11.32%	91.5%	28.7	27.1%
R8	n=2	26.7	2.00%	98.1%	27.2	24.7%
R9*	n=3	23.8	12.01%	104.0%	22.8	11.0%
R10*	n=3	15.6	26.18%	72.1%	21.6	18.0%
R11	n=3	9.45	8.12%	92.3%	10.2	8.80%
R14	n=3	28.3	16.32%	90.8%	31.1	8.16%

B. THg at the EERC

THg RESULT		FMSS Mean THg ug/m ³	FMSS Precision THg RSD or RPD	Accuracy THg %Rec	OH Mean THg ug/m ³	OH Precision THg RPD
ID	number (n) replicates					
R4	n=6	8.66	7.88%	103.8%	8.35	8.99%
R16	n=8	41.8	6.44%	89.7%	46.6	10.3%
R3*	n=4	8.07	11.2%	87.6%	9.21	6.08%
R12*	n=4	8.99	7.73%	86.1%	10.4	8.63%
R13*	n=4	36.3	6.15%	90.0%	40.3	10.37%
R15*	n=4	39.5	3.27%	101.4%	38.9	16.0%
R1	n=3	12.8	3.34%	NA	10.3	NA
R2	n=3	16.2	0.48%	NA	8.49	NA
R5	n=2	8.20	7.16%	112.9%	7.27	4.95%
R6	n=2	36.6	4.70%	108.3%	33.8	7.48%
R7	n=2	33.4	12.0%	94.0%	35.5	21.0%
R8	n=2	32.0	13.3%	91.9%	34.8	19.6%
R9*	n=3	24.4	12.2%	87.1%	28.0	30.6%
R10*	n=3	16.4	25.7%	70.3%	23.4	17.8%
R11	n=3	9.53	8.20%	89.3%	10.7	9.10%
R14	n=3	38.1	14.8%	94.6%	40.3	9.19%

C. Speciation at the EERC

%Hg ⁺² Result		FMSS Mean %Hg ⁺²	FMSS Precision %Hg ⁺² RSD or RPD	Accuracy %Hg ⁺² %rec	OH Mean %Hg ⁺²	OH Precision %Hg ⁺² RPD
ID	number (n) replicates					
R4	n=6	96.5%	1.1%	102.2%	94.4%	0.91%
R16	n=8	79.3%	1.9%	97.9%	81.0%	4.3%
R3*	n=4	93.2%	1.4%	99.0%	94.2%	1.0%
R12*	n=4	98.4%	0.5%	102.0%	96.5%	0.1%
R13*	n=4	78.6%	2.84%	99.4%	79.0%	1.4%
R15*	n=4	77.3%	4.8%	101.7%	76.0%	1.9%
R1**	n=3	0.184%	0.14%	NA	2.2%	NA
R2	n=3	87.0%	2.18%	NA	75.1%	NA
R5	n=2	95.7%	1.93%	102.2%	93.7%	0.33%
R6	n=2	88.7%	3.43%	107.5%	82.6%	10.0%
R7	n=2	78.6%	0.65%	97.6%	80.6%	6.2%
R8	n=2	83.7%	11.3%	107.4%	77.9%	5.2%
R9*	n=3	97.5%	0.16%	117.6%	82.9%	19.7%
R10*	n=3	95.0%	0.55%	102.5%	92.7%	0.2%
R11	n=3	99.2%	0.08%	103.4%	95.9%	0.30%
R14	n=3	74.1%	1.75%	95.8%	77.4%	1.04%

**Run 1 had Hg⁰ spikes only and had significant amounts of Hg⁰ (99.816%).
and the precision for Run 1 is as %Hgo.

Table V-2

FMSS AND OH PRECISION RESULTS BY RUN

A. Hg Species Concentration Result

FMSS MEAN	FMSS Mean	FMSS Mean	FMSS Mean	FMSS Mean	OH MEAN	OH Mean	OH Mean	OH Mean	OH Mean
	PHg	Hgo	Hg+2	THg		PHg	Hgo	Hg+2	THg
ID	ug/m3	ug/m3	ug/m3	ug/m3	ID	ug/m3	ug/m3	ug/m3	ug/m3
R4	0.0070	0.303	8.36	8.66	R4	0.255	0.465	7.88	8.35
R16	NA	8.74	33.1	41.8	R16	0.025	8.91	37.7	46.6
R3*	0.516	0.58	7.49	8.07	R3*	1.70	0.535	8.68	9.21
R12*	NA	0.14	8.84	8.99	R12*	0.010	0.360	10.1	10.4
R13*	NA	7.78	28.5	36.3	R13*	0.02	8.45	31.9	40.3
R15*	NA	8.96	30.5	39.5	R15*	0.04	9.38	29.6	38.9
R1	NA	12.8	0.0233	12.8	R1	0.02	10.05	0.23	10.3
R2	NA	2.10	14.1	16.2	R2	1.94	2.11	6.38	8.49
R5	0.079	0.347	7.86	8.20	R5	0.385	0.46	6.81	7.27
R6	0.599	4.14	32.5	36.6	R6	0.570	5.85	28.0	33.8
R7	0.104	7.15	26.3	33.4	R7	0.300	6.81	28.7	35.5
R8	0.91	5.32	26.7	32.0	R8	0.63	7.61	27.2	34.8
R9*	3.72	0.618	23.8	24.4	R9*	4.05	1.09	22.8	28.0
R10*	8.14	0.81	15.6	16.4	R10*	8.89	1.72	21.6	23.4
R11	NA	0.080	9.45	9.53	R11	0.040	0.435	10.2	10.7
R14	NA	9.8	28.3	38.1	R14	0.02	9.12	31.1	40.3

B. Mean Precision Result

PRECISION RESULT	FMSS	FMSS	FMSS	FMSS	PRECISION RESULT	OH	OH	OH	OH
	PHg	Hgo	Hg+2	THg		[pHg]	[Hgo]	[Hg+2]	THg
ID	RSD or RPD	RSD or RPD	RSD or RPD	RSD or RPD	ID	RPD	RPD	RPD	RPD
R4	71.3%	28.8%	7.98%	7.88%	R4	35.3%	6.45%	9.90%	8.99%
R16	NA	11.7%	5.61%	6.44%	R16	40.0%	28.5%	5.94%	10.3%
R3*	12.8%	31.3%	9.93%	11.2%	R3*	NA	9.35%	7.03%	6.08%
R12*	NA	36.3%	7.35%	7.73%	R12*	0.0%	5.56%	8.74%	8.63%
R13*	NA	11.2%	7.02%	6.15%	R13*	0.0%	5.21%	11.7%	10.4%
R15*	NA	15.2%	6.86%	3.27%	R15*	50.0%	22.0%	14.1%	16.0%
R1	NA	3.45%	70.2%	3.34%	R1	NA	NA	NA	NA
R2	NA	14.2%	2.65%	0.48%	R2	NA	NA	NA	NA
R5	53.5%	36.4%	9.09%	7.16%	R5	7.8%	0.00%	5.29%	5.0%
R6	NA	31.6%	1.27%	4.70%	R6	31.6%	40.2%	17.5%	7.5%
R7	41.0%	14.3%	11.3%	12.0%	R7	6.7%	4.85%	27.1%	21.0%
R8	NA	NA	2.0%	13.3%	R8	9.5%	1.3%	24.7%	19.6%
R9*	31.6%	18.5%	12.0%	12.2%	R9*	140.2%	32.3%	11.0%	30.6%
R10*	38.4%	17.5%	26.2%	25.7%	R10*	30.6%	15.7%	18.0%	17.8%
R11	NA	17.1%	8.12%	8.20%	R11	100.0%	16.1%	8.80%	9.10%
R14	NA	10.5%	16.3%	14.8%	R14	NA	12.7%	8.16%	9.19%

The first significant result from the tables is that the precision of either method did not vary much over the course of the 16 runs. The precision was generally similar for both the FMSS and simultaneous OH methods. The precision was worst at the lowest concentrations especially near method detection limits (For FMSS method MDLs, see section IV). Hg^0 concentrations during many of the runs were generally low relative to much larger concentrations of Hg^{+2} and in a few cases near the MDL (Runs 3, 10, 11, 12). Under these conditions, field blank and MDL considerations for both the FMSS and OH methods are more significant. In general PHg levels were also low, and in a few cases near MDL. However, in the few instances when the Hg on particulate flyash was significant, the precision of the PHg and other species concentrations remained quite good. This can be seen by the precision result for Run 9 and Run 10 (see Table V-2) during which time the ESP pollution control device was possibly malfunctioning.

The mean precision of the FMSS and OH replicates with and without testing by either method is summarized in Table V-3.

Table V-3
Precision Summary at the EERC

	PRECISION					PRECISION				
		FMSS	FMSS	FMSS	FMSS		OH	OH	OH	OH
		PHg	Hg ^o	Hg ⁺²	THg		[pHg]	[Hg ^o]	[Hg ⁺²]	THg
	RSD or RPD					RPD				
Quads No Tests	mean	71.3%	20.2%	6.80%	0.072	mean	37.6%	17.5%	7.92%	9.62%
	stdev	NA	12.1%	1.7%	0.010	stdev	3.3%	15.6%	2.8%	0.90%
Quad Ruggedness Tests*	mean	12.8%	23.5%	7.79%	0.071	mean	16.7%	10.5%	10.4%	10.3%
	stdev	NA	12.2%	1.4%	0.033	stdev	28.9%	7.9%	3.1%	4.2%
Replicates Natural Gas	mean	NA	8.81%	36.4%	1.91%	mean	NA	NA	NA	NA
	stdev	NA	0.076	0.5	0.020	stdev	NA	NA	NA	NA
Additional Ruggedness **High PHg	mean	35.0%	18.0%	19.1%	18.9%	mean	85.4%	24.0%	14.5%	24.2%
	stdev	4.8%	0.7%	10.0%	9.6%	stdev	77.5%	11.7%	4.9%	9.0%
Replicates No Ruggedness Duplicates and Triplicates	mean	47.3%	22.0%	8.02%	10.0%	mean	31.1%	12.5%	15.3%	11.9%
	stdev	8.9%	11.3%	5.7%	3.9%	stdev	39.9%	15.0%	9.2%	6.7%

A significant result is that the precision of the duplicates by either the FMSS method or the OH method was fairly similar, except during the ruggedness tests when the precision of the Hg^0 was worse. Again, however, the Hg^0 levels were often quite low during these runs making field blank considerations more significant.

Although it is difficult to draw significant conclusions by comparing precision RSD ($n > 2$) and RPD ($n = 2$), it is possible to make general comparisons. One result is that in general the precision of the FMSS duplicates, triplicates, quadruplicates were quite similar. Also, the precision of the quadruplicates with no testing was similar to the precision during the FMSS ruggedness tests. Based on the replicates with no additional ruggedness at the EERC (Table V-3), it is concluded that the mean precision of the FMSS method as determined under real conditions for duplicates and triplicates was $\pm 47\%$ for PHg, $\pm 22\%$ for Hg^0 , $\pm 8\%$ for Hg^{+2} , and $\pm 10\%$ for THg. The mean precision of the FMSS method was $\pm 6.5\%$ for $\%\text{Hg}^{+2}$ or the percent oxidized Hg of the total (THg+PHg).

The FMSS precision can best be seen from the graphs Figure V-1. These graphs include A) FMSS Precision versus Hg concentration and the precision of both the FMSS and OH methods for B) THg and C) %Hg⁺² for each run at the EERC.

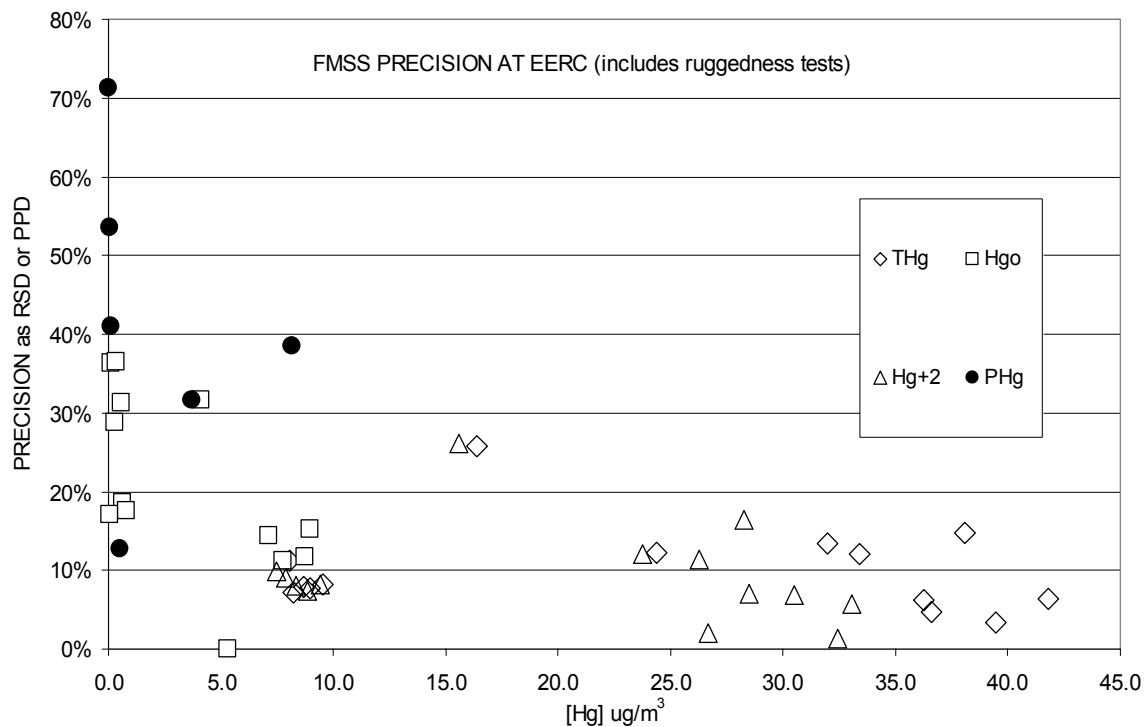


Figure V-1 A.

FMSS Precision versus Hg concentration

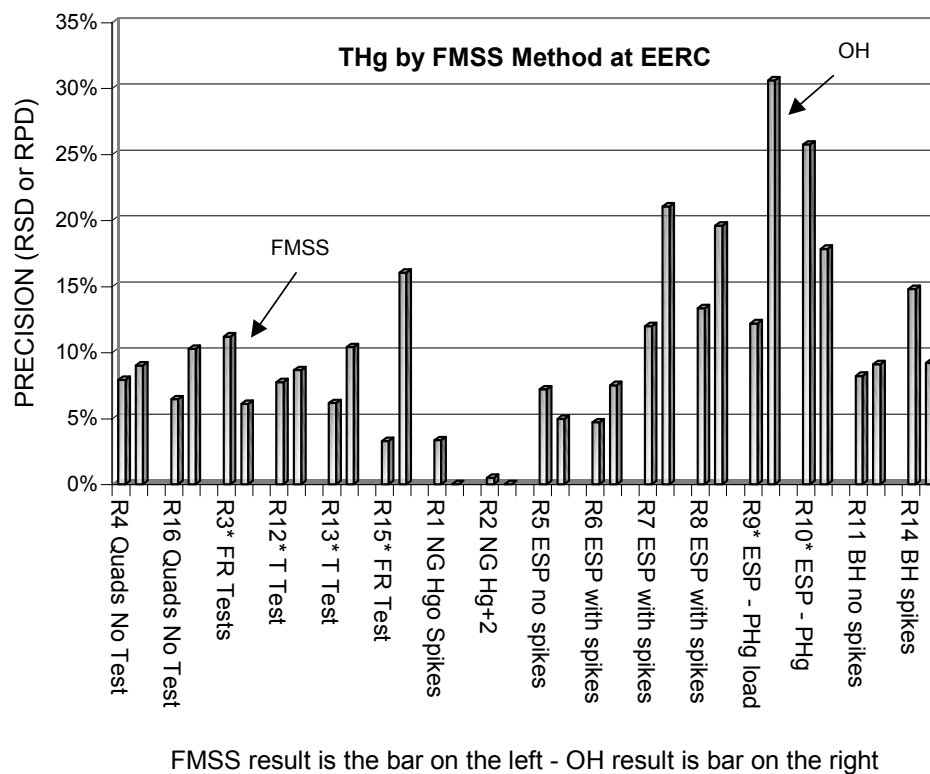


Figure V-1 B.

Precision of THg verses EERC run for different fluegas conditions.

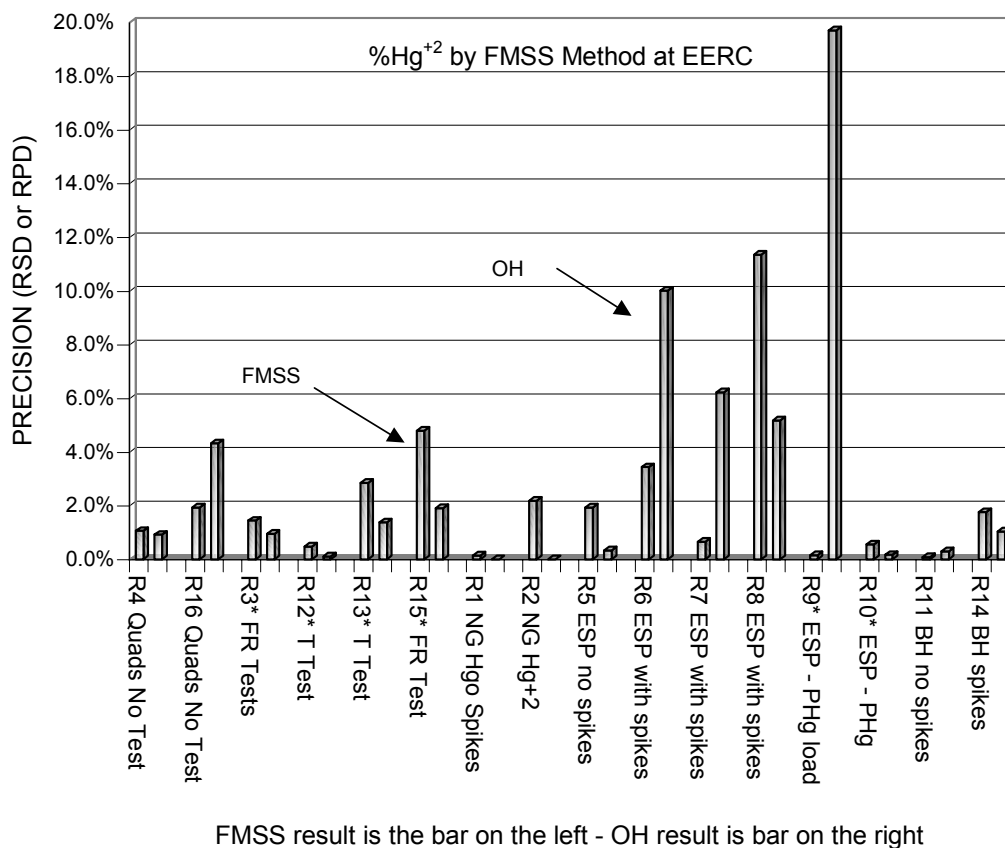


Figure V-1 C.

Precision of Hg⁺² verses EERC run for different fluegas conditions

The significant result as evidenced in precision graphs is that FMSS precision was almost always better than 20%. This was true despite the ruggedness testing and concentrations near MDL. The worst precision of 25% was during Runs 9 and 19 when the ESP was malfunctioning and particulate loads were abnormally high. However, during these same runs the OH precision was also worse.

V.B Accuracy – Comparison to established OH method.

The accuracy of the means of the FMSS and OH methods can best be seen from Figure V-2.

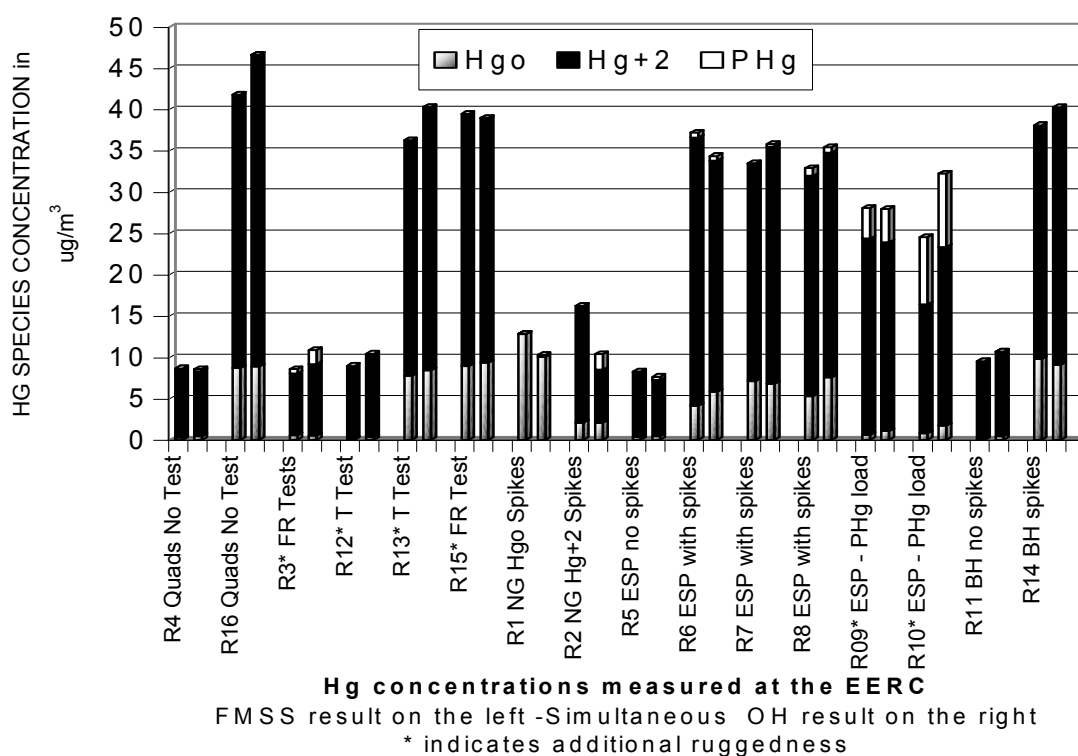


Figure V-2.

FMSS and OH comparison of the means

The mean PHg, Hg⁰ and Hg⁺² species concentrations are combined in a single bar for both the FMSS and OH method replicates. The bar on the left represents the FMSS method result; the bar on the right represents a separate determination by the OH method. The height of the bar represents the total Hg in the sample and is the sum of the total vapor phase Hg⁰ and Hg⁺² and any Hg collecting in the particulate phase (or THg+PHg). That the THg+PHg result by the FMSS and OH method was sometimes higher and sometimes lower, this indicated that slight differences between the methods exist, but that there was generally no significant biases. For a complete discussion of bias see section V-C.

Good agreement of the means was observed almost all cases. The accuracy was worst during Runs 9 and 10 which had abnormally high particulate (3-10ug/m³) and for Hg⁰ concentrations whose concentrations were generally quite low, and made in the presence of much larger concentrations of Hg⁺². Under these conditions, field blank and MDL considerations for both the FMSS and OH methods are more significant.

The accuracy of the FMSS result relative to the OH method was presented for each species (PHg, Hg⁰, Hg⁺²) concentration for THg and %Hg⁺² in Table V-1. Presented here is the accuracy expressed for comparison purposes as the means of the accuracy of the replicates, with and without additional ruggedness. This result is shown in Table V-4.

Table V-4
Accuracy Summary at the EERC

ACCURACY SUMMARY		PHg % rec	[Hg ⁰] % rec	[Hg ⁺²] % rec	THg % rec	% Hg ⁺² % rec
Quads No Tests	mean	NA	81.6%	96.9%	96.7%	100.1%
	stdev	NA	23.3%	12.9%	9.9%	3.0%
Quad Ruggedness Tests*	mean	30.4%	83.9%	91.7%	91.3%	100.5%
	stdev	NA	30.3%	7.8%	6.9%	1.54%
Replicates Natural Gas	mean	NA	NA	NA	NA	NA
	stdev	NA	NA	NA	NA	NA
Additional Ruggedness **High PHg	mean	91.7%	52.2%	88.0%	78.7%	110.1%
	stdev	0.2%	6.7%	22.6%	11.9%	10.7%
Replicates No Ruggedness	mean	76.3%	74.5%	100.7%	98.5%	102.3%
	stdev	58.9%	32.3%	11.9%	9.6%	4.9%

On average, the accuracy (as %Rec= mean_{FMSS} / mean_{OH}) of the FMSS with the OH method was 100±3% for Hg⁺², THg, and %Hg⁺²; and 100±25% for Hg⁰ and PHg. However, the result for Hg⁰ and PHg included many cases when the concentration was quite low.

The accuracy of the FMSS relative to the OH method can best be seen in Figure V-3. Figure V-3 shows the accuracy (y-axis) relative to Hg concentrations (x-axis) and includes data from all 16 runs at the EERC, including the ruggedness tests.

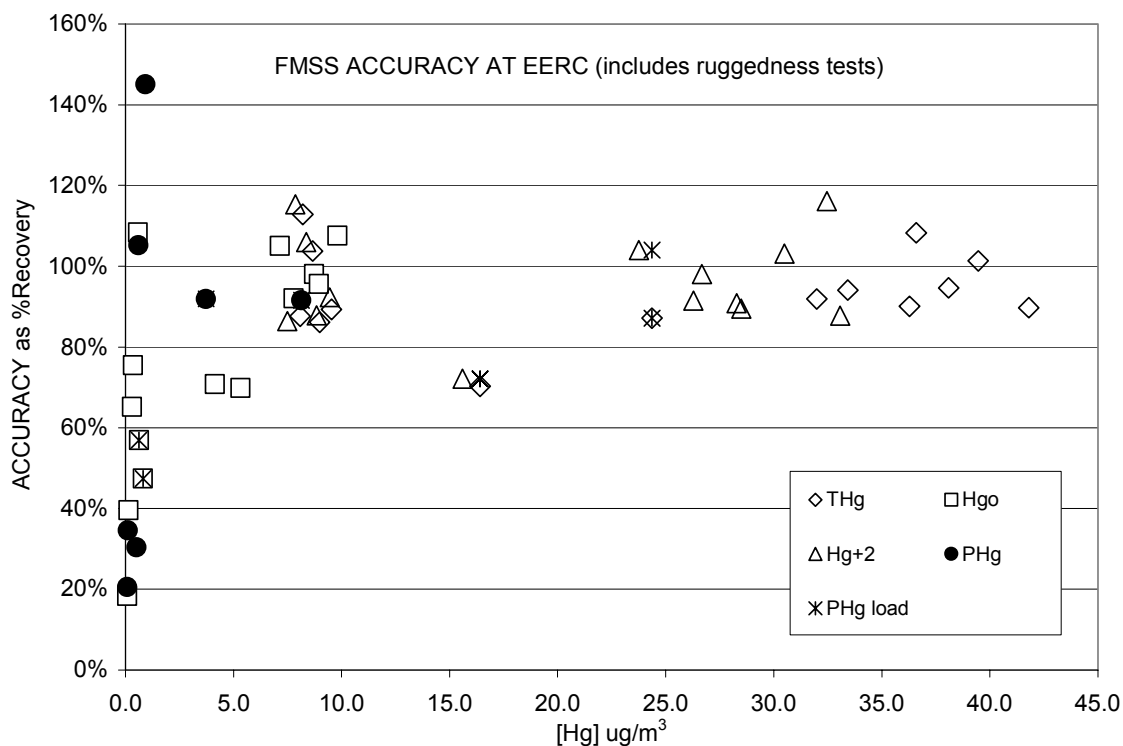


Figure V-3

FMSS-OH % recovery verses mean Hg concentration at the EERC.

When values near the MDL are not considered, the accuracy of the FMSS was better than $\pm 20\%$ for all species for the range of conditions in Table V-1. This was true even for the ruggedness tests, including those with abnormally high particulate levels.

V. Bias – Comparison of all FMSS and OH results.

The bias between the FMSS and OH methods for the measurement of Hg species concentrations is summarized in Table V-5. This bias was determined under real conditions at the EERC for the whole range of fluegas conditions (see condition, Table V-1).

Table V-5

FMSS –OH Bias Summary at the EERC

BIAS Graph Data	PHg	Hg ⁰	Hg ⁺²	THg	THg+PHg	%Hg ⁺²
Slope or Bias	1.075	0.839	1.070	1.120	1.118	84.4%
y-int (ug/m ³)	0.07	0.9177	-1.61	-3.127	-2.979	51.0%
R ²	0.9953	0.9143	0.93	0.9602	0.9582	85.1%
FMSS Error Bar	47.3%	22.0%	8.02%	10.0%	10.0%	4.0%
OH Error Bar	31.1%	12.5%	15.3%	11.9%	11.9%	3.5%

The bias was calculated from the slopes of the plots of the mean Hg species concentration for the FMSS method (X-axis) with the simultaneous result by the OH method (Y-axis). The plots for %Hg⁺², THg, Hg⁺² and Hg⁰ can be seen in Figure V-4. The error bars in the figure (shown in Table V-5) are the precision of the means for the FMSS and OH methods for replicates with no ruggedness. A slope of 1.00 indicates perfect agreement between the methods and no bias. The figure includes data for the entire 16 Runs at the EERC, including several results near the method detection limits and results from runs that underwent additional ruggedness testing.

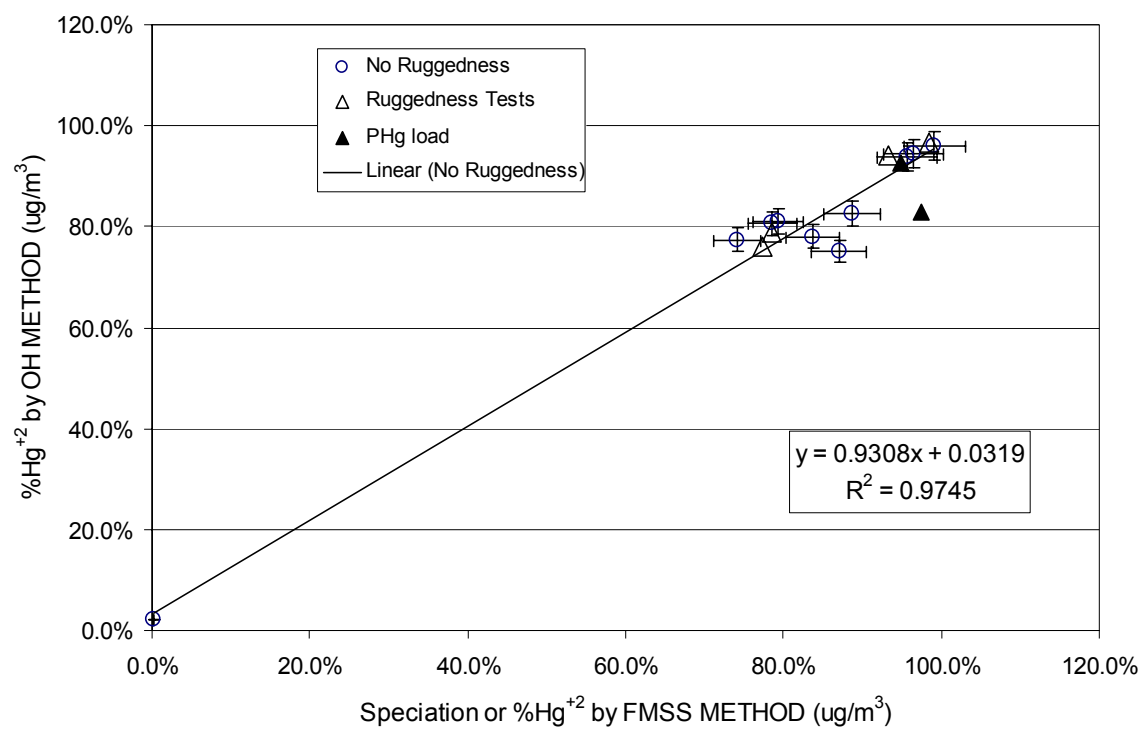


Figure V-4 A

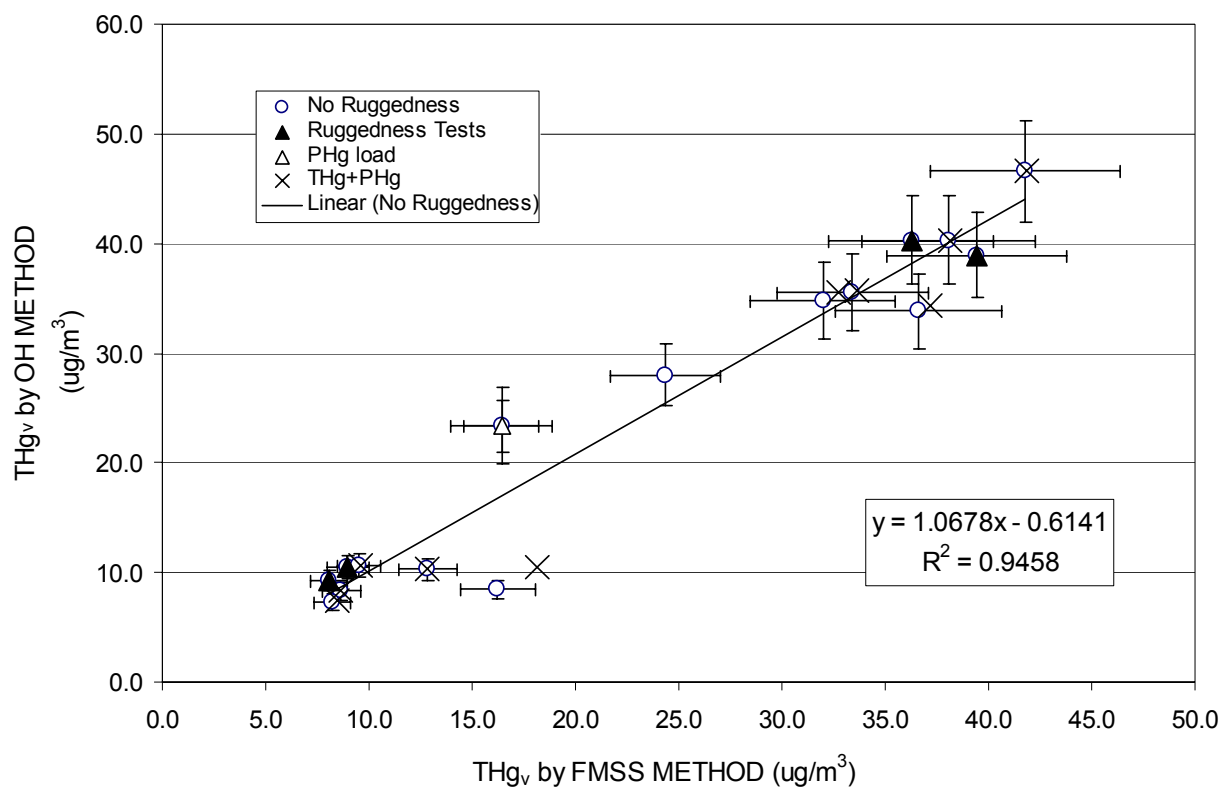


Figure V-4 B

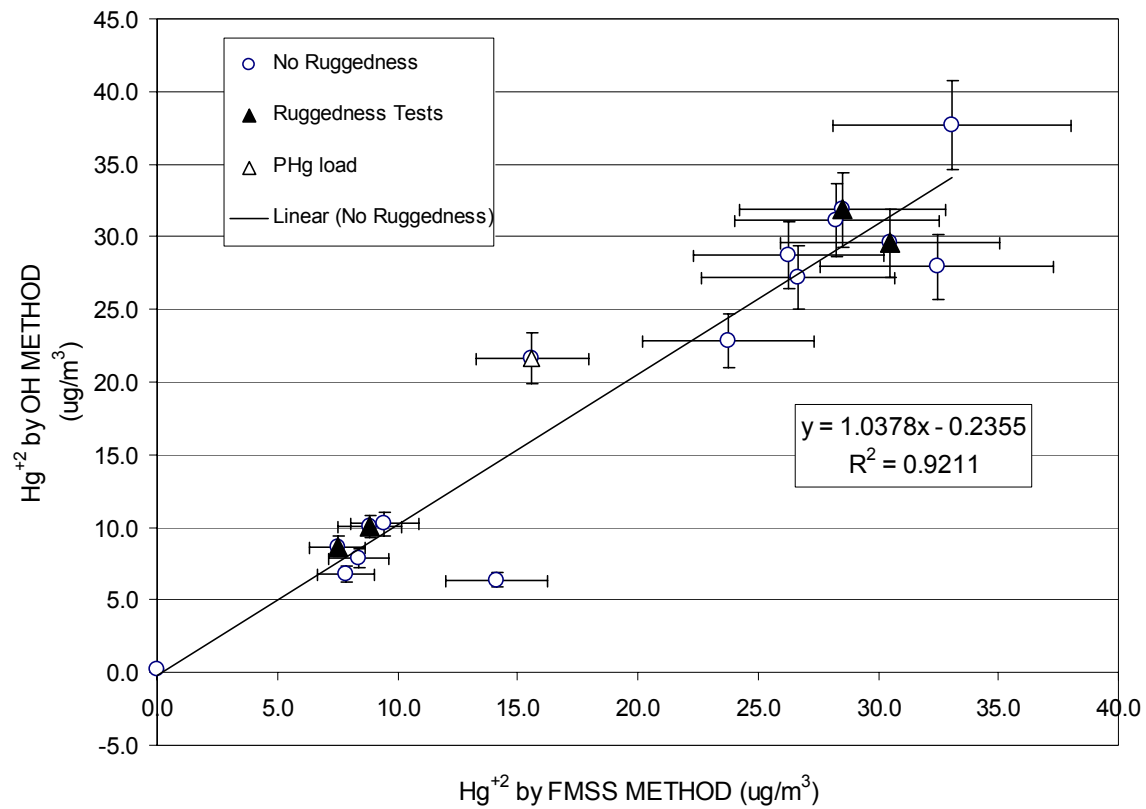


Figure V-4 C

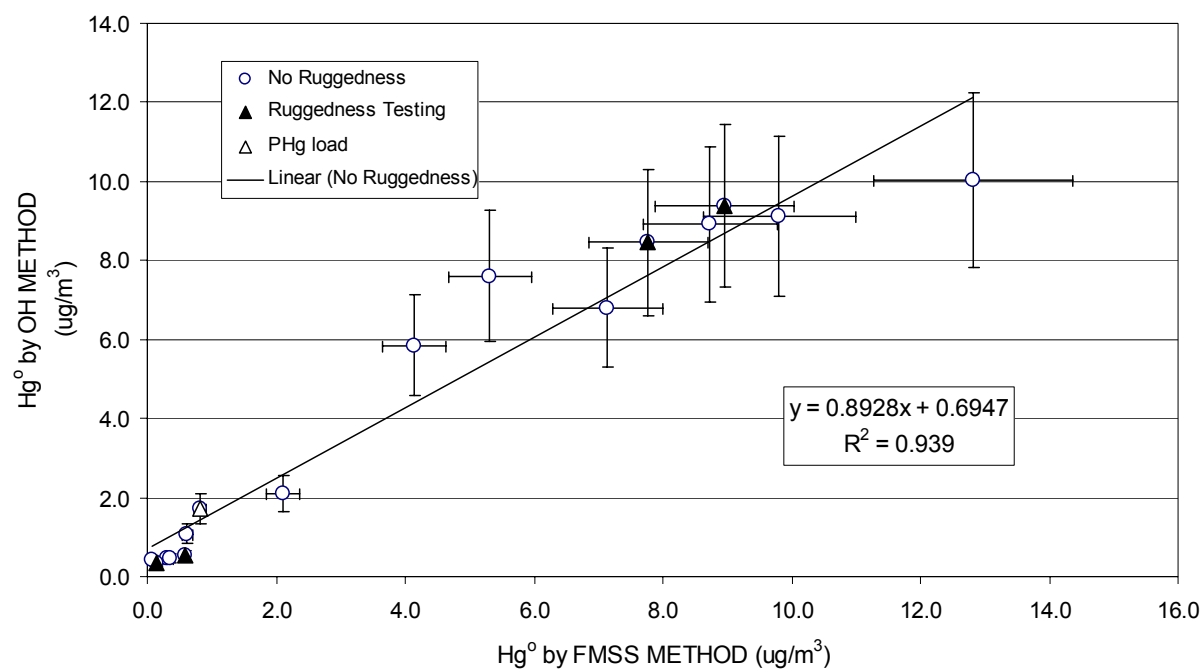


Figure V-4 D

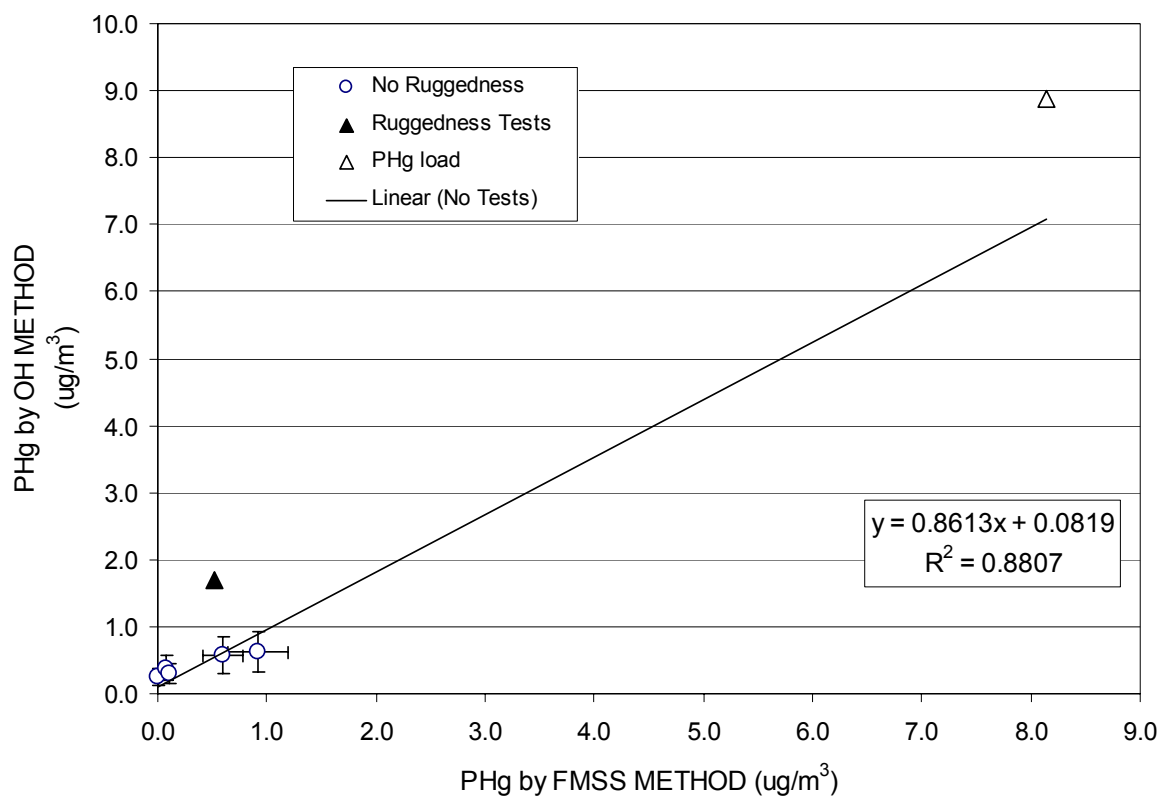


Figure V-4 E

VI. Ruggedness Testing at the EERC

Tests for FMSS ruggedness were an important part of the PBMS. A detailed discussion of each ruggedness test is provided in the following section.

VI. A Quadruplicate Temperature Tests

The importance of the sampling probe temperature to Hg determination was investigated during two quadruplicate temperature tests (Runs 12 and 13). During these runs, four parallel samples were collected that were identical except that probe temperature was varied from 75 to 105°C. This represented ruggedness that is one to three times the ideal FMSS range.

The precision and accuracy results of the temperature tests are shown in Table VI-1.

Table VI-1
Precision and Accuracy during temperature tests

RUN 12 TEMPERATURE TEST						
FMSS Sample ID	Temp C	PHg ug/m ³	Hg ⁰ ug/m ³	Hg ⁺² ug/m ³	THg ug/m ³	%Hg ⁺²
FMS-5-031500	75.67	nc	0.101	8.39	8.49	98.8%
FMS-6-031500	88.44	nc	0.209	9.31	9.52	97.8%
FMS-7-031500	96.41	nc	0.102	8.19	8.29	98.8%
FMS-8-031500	105.7	nc	0.157	9.49	9.65	98.4%
FMSS MEAN	91.6	NA	0.158	8.85	9.00	98.3%
STDEV	12.7	NA	0.052	0.65	0.69	0.46%
% RSD	13.9%	NA	32.7%	7.3%	7.7%	0.46%
OH MEAN		0.01	0.36	10.1	10.4	96.4%
OH %RPD		0.0%	5.6%	8.74%	8.71%	0.03%
ACCURACY FMSS-OH (%REC)		NA	43.8%	88%	86%	101.9%
RUN 13 TEMPERATURE TEST						
FMSS Sample ID	Temp C	PHg ug/m ³	Hg ⁰ ug/m ³	Hg ⁺² ug/m ³	THg ug/m ³	%Hg ⁺²
FMS-1-031600	75.28	nc	8.10	31.4	39.5	79.5%
FMS-2-031600	86.67	nc	8.33	27.5	35.9	76.8%
FMS-3-031600	96.56	nc	6.47	28.1	34.6	81.3%
FMS-4-031600	105.9	nc	8.20	27.0	35.2	76.7%
FMSS MEAN	91.11	NA	7.78	28.50	36.28	78.6%
STDEV	13.17	NA	0.87	2.00	2.23	2.23%
% RSD	14.5%	NA	11.2%	7.0%	6.1%	2.8%
OH MEAN		0.02	8.45	31.9	40.3	79.0%
OH %RPD		0.0%	5.2%	11.7%	10.4%	1.38%
ACCURACY FMSS-OH (%REC)		NA	92.0%	89%	90%	99.5%

The results of the temperature tests can perhaps best be seen in Figures VI-1.

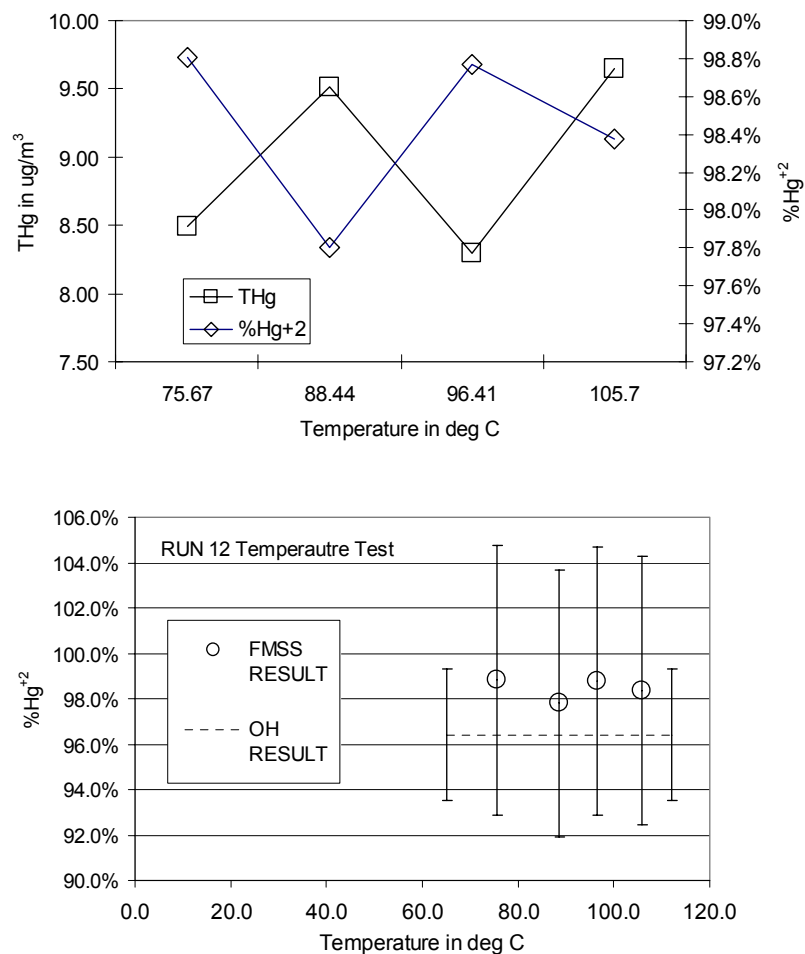


Figure VI-1 A

Quad Temperature Test Run 12

Temperature during Run 12 samples represented twice to three times the ideal range (top figure). Despite the additional ruggedness, the precision of the %Hg⁺² FMSS method (error bar on point) was similar to that of the OH method (error bars on line) and the accuracy of the %Hg⁺² was 102%. The worst precision and accuracy was for Hg⁰ (see RSD, Table VI-1) when Hg was at near blank levels.

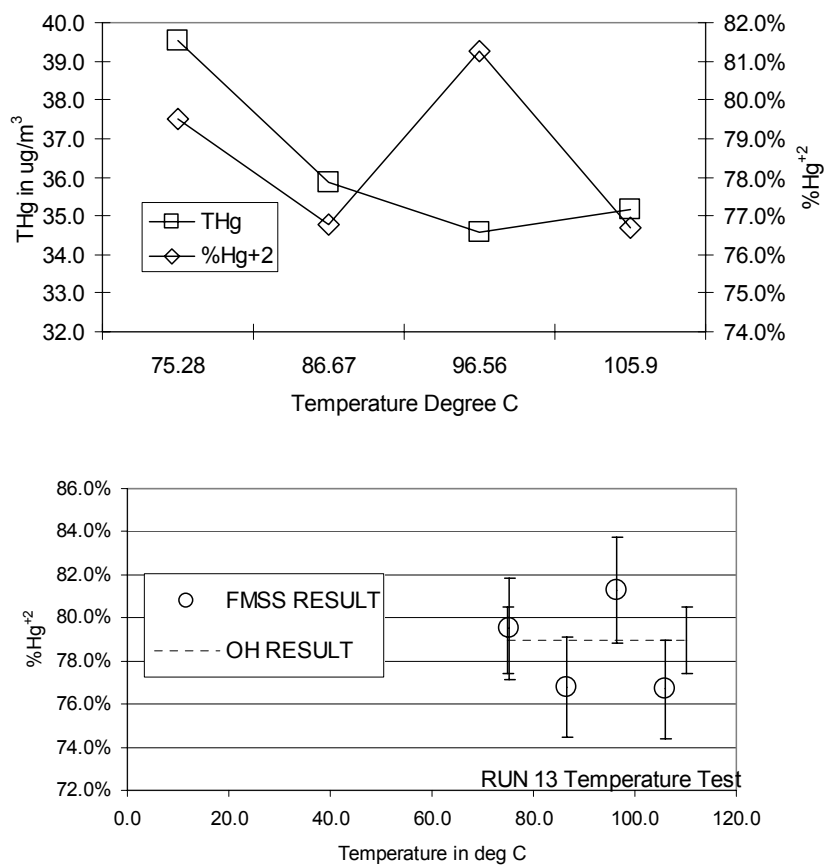


Figure V-1 B.

Quad Temperature Test Run 13

Temperatures during Run 13 ranged from 75 to 105 °C, about three times above the control range. However, despite the additional ruggedness, the precision of the FMSS method (error bar on point) was similar to that of the OH method (error bar on line) and the accuracy of the %Hg⁺² was 99.4%.

VI. Quadruplicate Flow Rate Tests

The importance of flowrate to Hg determinations was evaluated during two quadruplicate flowrate ruggedness tests during Runs 3 and 15. During these runs four parallel samples were collected that were identical except the collection flow rates was varied from 0.25 to 0.85 slpm.

The precision and accuracy results of the flowrate tests are shown in Table VI-2.

Table VI-2

Precision and Accuracy during flowrate tests

RUN 3 FLOWRATE TEST						
FMSS	Flow Rate	PHg	Hg ⁰	Hg ⁺²	THg	%Hg ⁺²
Sample ID	slpm	ug/m ³	ug/m ³	ug/m ³	ug/m ³	
FMSS-1-030800**	0.22	na	0.622	9.82	10.44	94.0%
FMSS-2-030800	0.44	0.47	0.494	7.62	8.12	93.9%
FMSS-4-030800**	0.44	na	0.457	6.69	7.15	93.6%
FMSS-3-030800	0.57	0.56	0.787	8.16	8.95	91.2%
MEAN (including **)	0.417	0.516	0.590	8.075	8.665	93.2%
(n=4) STDEV	0.141	0.066	0.149	1.313	1.396	1.3%
% RSD	33.9%	12.8%	25.3%	16.3%	16.1%	1.4%
OH MEAN						
		1.7	0.535	8.7	10.1	86.7%
%RPD						
		NA	9.3%	7.03%	11.3%	18.3%
ACCURACY FMSS-OH (%REC)*						
		30.4%	110%	93.1%	86.1%	107.5%
RUN 15 FLOWRATE TEST						
FMSS	Flow Rate	PHg	Hg ⁰	Hg ⁺²	THg	%Hg ⁺²
Sample ID	slpm	ug/m ³	ug/m ³	ug/m ³	ug/m ³	
FMSS-9-031600	0.24	na	8.44	32.41	40.85	79.3%
FMSS-10-031600	0.47	na	7.36	32.14	39.51	81.4%
FMSS-11-031600	0.60	na	9.52	28.21	37.73	74.8%
FMSS-12-031600	0.88	na	10.5	29.24	39.76	73.6%
FMSS MEAN	0.548	NA	8.960	30.501	39.462	0.773
STDEV	0.267	NA	1.360	2.093	1.291	0.037
% RSD	48.8%	NA	15.2%	6.9%	3.3%	4.8%
OH MEAN						
		0.04	9.38	29.6	39.0	75.9%
OH %RPD						
		50.0%	22%	14.1%	15.9%	1.83%
ACCURACY FMSS-OH (%REC)						
		NA	96%	103%	101%	101.8%

The results of the flowrate tests can perhaps best be seen in Figures VI-2.

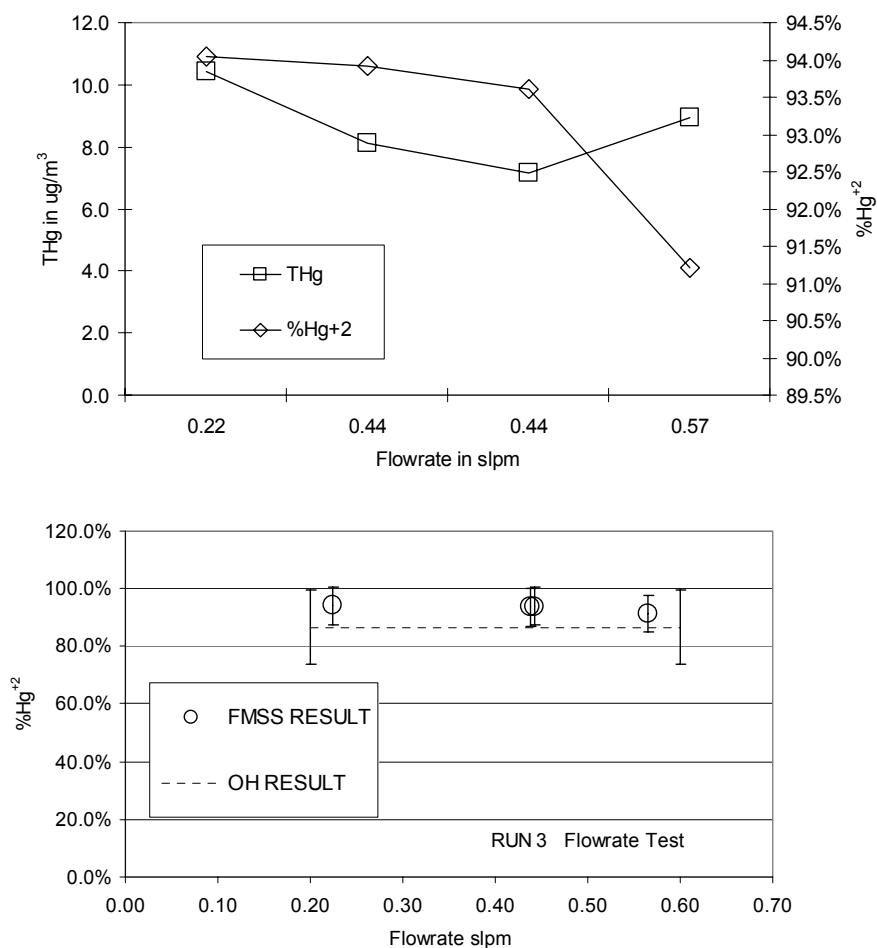


Figure VI-2 A

Quad Flowrate Run 3

Flowrates for Run 3 ranged from 0.2 to 0.6 slpm and represented twice the ideal range. Run 3 had additional ruggedness. Heavy particulate noted on all samples, condensation was noted on the sample with the lowest flowrate, indicating possible failure to maintain temperature control, and attempts to maintain the 0.8 slpm flowrate failed thus spanning a whole range of flowrates in a single sample. FMSS precision (error bar) was similar to OH precision (error bars of the line). The accuracy relative to the OH result was worse than normal but still better than 10% with a percent recovery (relative to OH) for %Hg⁺² of 107%.

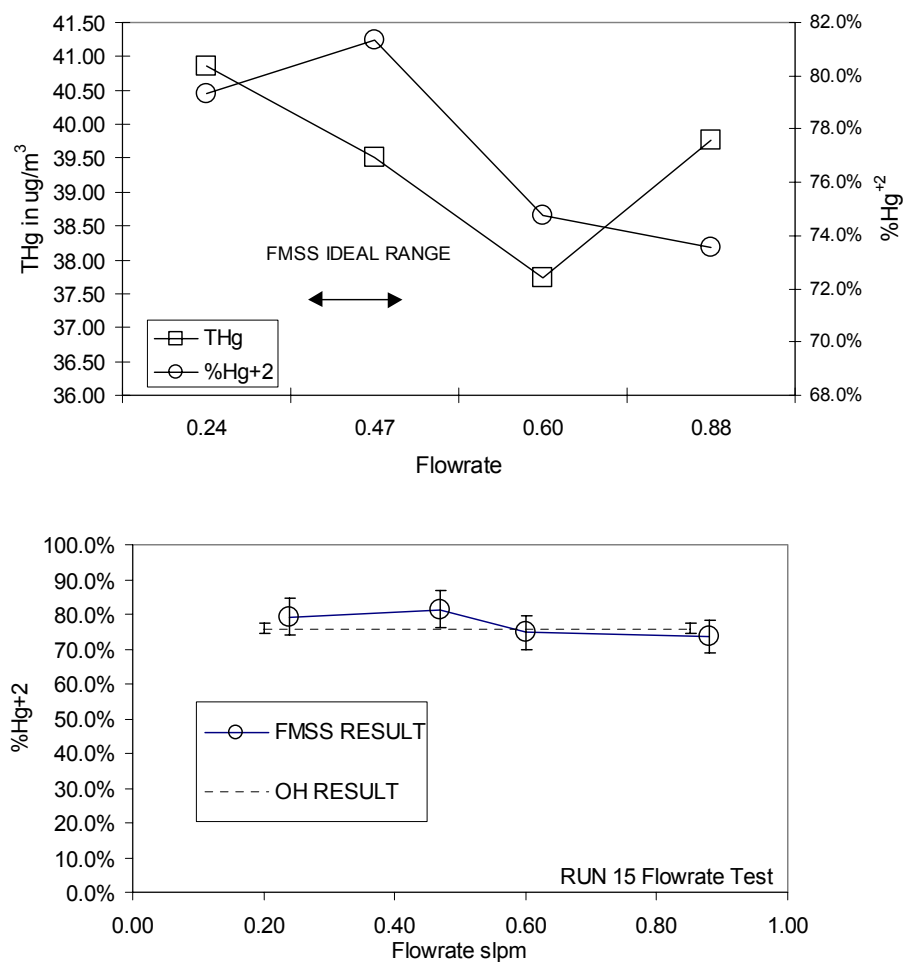


Figure VI-2 B

Quad Flowrate Test Run 15

Flowrates during Run 15 ranged from 0.8 to 0.2 slpm and represented four times the ideal range. Despite the ruggedness, the precision of the FMSS method was similar to the OH method, and there was good agreement between the two methods. The accuracy of $\%Hg^{+2}$ was 102%.

The actual control used at the EERC (in RSD) during normal operation of the FMSS method was defined earlier and was $\pm 6\%$ for temperature and $\pm 3\%$ for flowrate. During ruggedness tests variations in temperature were $\sim 14\%$ and in flowrate were $\sim 30\text{-}50\%$ (See Table VI-1 and VI-2). This is roughly two to four times the normal control range.

Despite the additional ruggedness, the precision and accuracy of the FMSS remained quite good and was similar to that of the OH methods duplicates. And no significant trends were observed between the measured Hg concentrations and flowrate or temperature.

In conclusion, based on the good result at the EERC for FMSS precision and accuracy during the ruggedness tests, the FMSS method is expected to be very reliable method for measuring total and speciated mercury in coal fluegas matrices.

VII. Interferences

The samples collected at both the EERC and the DOE reflect matrices of natural gas and coal fluegas matrices with SO_2 and HCl. As such, the results of this study include interferences from SO_2 , NO_x , HCl, Flyash and other components of fluegas and were an integral part of the experiments.

VIII. Matrix Suitability

The application of the FMSS to measurements of total mercury has in the past (see historical studies, section II) shown more than adequate performance. This study was applied at the EERC, mainly for coal matrices, for the range of conditions presented in Table VIII-1.

Table VIII-1

Range of applicable matrices tested under real conditions at the EERC

HG CONCENTRATIONS STUDIED AT EERC							
Overall range all runs*	PHg ug/m ³	Hg ⁰ ug/m ³	Hg ⁺² ug/m ³	THg (v) ug/m ³	THg+PHg ug/m ⁴	fraction as vapor	%Hg ⁺² ***
MDL**	0.006	0.026	0.018	0.035			
lowest measured [Hg]	0.010	0.251	0.127	7.737	7.969	0.70	1.21%
highest	8.5	11.4	35.4	44.2	44.2	1.00	97.5%
mean of range	1.03	3.98	16.9	21.0	24.6	0.96	81.4%
stdev of range (mean +/-1 stdev)	2.17	4.11	12.2	15.0	13.7	0.08	22.8%
lower limit of applicable range	0.01	0.03	4.73	6.01	10.96	0.88	58.6%
upper limit of applicable range	3.21	8.08	29.16	36.06	38.30	1.04	104.2%

* The ranges of Hg concentrations covered a factor >6

**MDL was based on MDL-A and MDL-B Result

***%Hg+2 is the percent of the THg+PHg

Based on the results of this study, it is argued here that the FMSS method is suitable for future applications under real conditions in similar matrices. It is expected that the FMSS method will be applicable to other fluegas matrices, such as from municipal waste incinerators, sewage sludge incinerators, smelting and other high temperature or combustion processes. However, the limitations of this study are for coal fluegas only.

IX. Laboratory Reproducibility

One important aspect of the PBMS is to collect samples in different fluegas systems, coal type, sampling technicians and analysis technicians. Therefore, to address the question of: "Can multiple operators and multiple laboratories obtain comparable data?" The answer is yes based on a brief inter-comparison of the FMSS and OH methods that was applied at the DOE. Results of this inter-comparison can be seen in Figure IX-1 in which the Hg concentration in $\mu\text{g}/\text{m}^3$ (y-axis) is shown for the FMSS method (left bar) and for the OH method (right bar) for each run at the DOE.

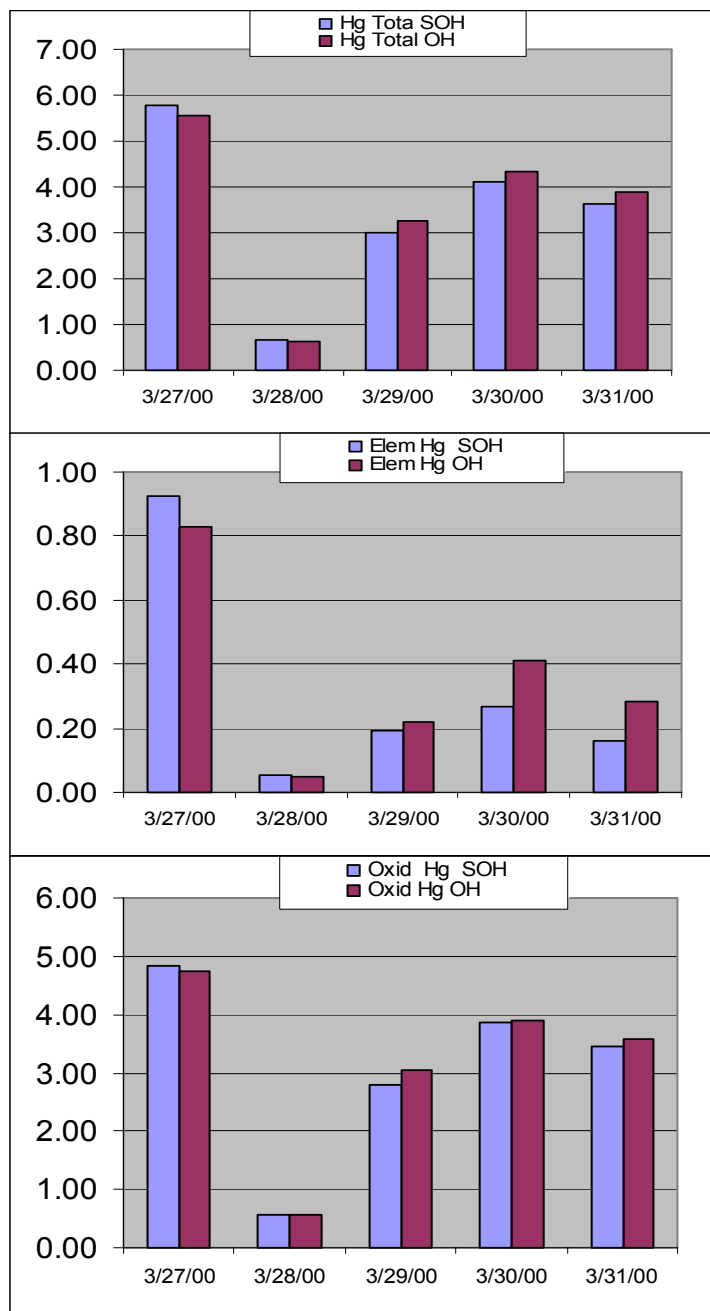


Figure IX-1 Intercomparison at another site (DOE)

Note: FMSS Method Result is indicated as SOH for the "sorbent" method that is similar to OH

FMSS precision during this brief inter-comparison ranged from 0.8% to 8.4% (RPD) which was excellent considering that the data was collected by people trained to operate (albeit a simple system) for essentially a 2 hour session. This again demonstrates the robustness of the technique and shows that field operators can be trained to perform clean techniques easily in the field.

X. Conclusions

The FMSS method was evaluated relative to the Ontario Hydro (OH) Method at the Energy and Environment Research Center (EERC) and again briefly at the US DOE for a variety of fuels, ash loadings, and pollution control methods. The evaluation included numerous ruggedness tests using quadruplicate sampling devices, both with and without species specific (Hg^0 and Hg^{+2}) spiking.

The FMSS method exhibited very good precision with a mean relative percent difference (RPD) of $\pm 22\%$ for Hg^0 , $\pm 8\%$ for Hg^{+2} , $\pm 10\%$ for THg, and $\pm 6.5\%$ for $\% \text{Hg}^{+2}$ or the percent oxidized Hg of the total (THg+PHg). The FMSS exhibited good agreement with OH methods and accuracy was better than $\pm 20\%$ for all species for the range of conditions in this study, including during ruggedness tests. The mean accuracy of the duplicates and the triplicates for the FMSS method was better than 97% for Hg^{+2} , THg, and $\% \text{Hg}^{+2}$. Based on the results presented here, the FMSS method is expected to be very reliable, even in the presence of SO_2 , NO_x , HCl, and flyash.

Based on the results of this PBMS, we conclude the FMSS Method is equivalent to the ASTM approved OH Method and a therefore a valid method for the determination of total Hg, PHg, gaseous Hg^{+2} and Hg^0 concentrations in a flue gas matrix. Considering many factors, including simplicity, lack of hazardous solutions in the field, precision, sensitivity, accuracy and cost, the FMSS method has many advantages that make it a viable choice for the measurement total and speciated mercury in coal fluegas.

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Appendix A

SUMMARY OF ALL THE FMSS AND OH RESULTS AT THE EERC

FIELD BLANKS		Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result									
RESULT	PHg	KCLA	KCLB	ICA	T-Vol	[pHg]	[Hg ⁰]	[Hg ⁺²]	[THg]		
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter	ug/m ³	ug/m ³	ug/m ³	ug/m ³		
FMS-9-030700 FB	nc	0.1473	0.0859	0.145	30.0	na	0.0048	0.0078	0.0126		
FMS-13-030700 FB	nc	2.78	0.0205	0.015	30.0	na	0.0154	0.0029	0.0183		
FMS-3-031000 FB	0.0419	0.0395	0.0000	0.490	30.0	0.0014	0.0163	0.0013	0.0177		
FMS-5-031300 FB	na	0.3990	0.0000	0.377	30.0	na	0.0126	0.0000	0.0126		
FMS-4-031400 FB	0.0239	0.0000	0.0000	0.416	30.0	0.0008	0.0139	0.0000	0.0139		
FMS-8-031400 FB	0.132	0.0356	0.0823	0.371	30.0	0.0044	0.0124	0.0039	0.0163		
FMS-4-031500 FB	nc	0.0000	0.0000	0.640	30.0	na	0.0213	0.0000	0.0213		
FMS-8-031600 FB	nc	0.2026	0.0000	0.789	30.0	na	0.0263	0.0068	0.0330		
2.78t-test											
n=8											
						FMSS mean	0.0022	0.0154	0.0028	0.0182	
						STDEV	0.0019	0.0064	0.0031	0.0067	
						MDL-A	0.0058	0.0192	0.0093	0.0202	
One KCLA value was removed by t-test and replaced by mean.											

CLEAN NATURAL GAS FLUEGAS MATRIX BLANK										Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Results			
RESULT	PHg	KCLA	KCLB	ICA	T-Vol	[pHg]	[Hg ⁰]	[Hg ⁺²]	THg				
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter	ug/m ³	ug/m ³	ug/m ³	ug/m ³				
FMS-1-030600	inval	0.675	0.000	1.45	26.7	na	0.0390	0.0224	0.0615				
FMS-3-030600	nc	0.020	0.102	1.23	30.9	na	0.0246	0.0011	0.0257				
FMS-4-030600	nc	0.123	0.123	1.52	31.2	na	0.0335	0.0050	0.0385				
FMS-1-030700	nc	0.225	0.000	0.697	28.7	na	0.0089	0.0050	0.0139				
FMS-2-030700	nc	0.000	0.123	0.944	30.3	na	0.0158	0.0012	0.0170				
FMS-3-030700	nc	0.286	0.164	0.726	22.0	na	0.0176	0.0176	0.0353				
FMS-4-030700	nc	0.082	0.000	0.784	31.2	na	0.0098	-0.0002	0.0096				
FMS-5-030700	nc	0.000	0.020	1.16	30.7	na	0.0225	-0.0022	0.0203				
					Flowrate RSD								
					11.1%								
EERC Run 0		3/6/00-3/7/00				FMSS mean		NA	0.0215	0.0063	0.0277		
n=8		Natural Gas		No spikes		STDEV		NA	0.0107	0.0089	0.0169		
					See MDL-B Calculation	NA	0.032	0.027	0.051				

COAL FLUEGAS MATRIX MID LEVEL NO SPIKES

RESULT FMSS SAMPLE ID	PHg ng/trap	KCLA ng/trap	KCLB ng/trap	ICA ng/trap	T-Vol corr., liter	Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result						
						[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³	%Hg ⁺² THg+PHg
FMS-5-030800	0.055	150.3	0.368	8.85	19.3	0.0006	0.443	7.79	8.24	94.5%	8.24	94.6%
FMS-6-030800	0.21	181.3	0.368	6.01	20.2	0.0081	0.282	8.98	9.26	96.9%	9.27	97.0%
FMS-7-030800	0.10	149.6	0.182	4.22	19.5	0.0031	0.201	7.69	7.89	97.4%	7.90	97.5%
FMS-8-030800	inval	175.1	0.306	5.76	19.6	na	0.279	8.97	9.24	96.9%	9.25	97.0%
FMS-9-030800	0.29	181.3	0.678	7.74	20.3	0.0119	0.365	8.95	9.31	96.0%	9.32	96.1%
FMS-10-030800	0.27	152.1	0.000	5.15	19.6	0.0113	0.247	7.76	8.00	96.8%	8.01	96.9%
FMS-11-030800	26.02	26.0	0.492	48.10	15.0	4.74	3.20	4.77	4.97	35.5%	4.97	35.6%
FMS-12-030800	33.06	45.2	0.461	26.76	20.5	4.61	4.29	0.76	2.05	37.0%	2.05	37.1%
					Flowrate RSD							
					9.29%							

Flowrate RSD 9.29%

EERC Run 4

3/8/2000-18:37
n=6
Bitcoal ESP with spikes
See MDL-C Calculation
Quads No Tests

FMSS Mean	0.0070	0.303	8.36	8.66	96.4%	8.67	96.5%
STDEV	0.0050	0.087	0.667	0.682	1.0%	0.682	1.02%
FMSS Precision	71.3%	28.8%	8.0%	7.9%	1.1%	7.9%	1.1%

Ontario Hydro Simultaneous Result

OH SAMPLE ID	[pHg]	[Hg ⁰]	[Hg ⁺²]	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³	%Hg ⁺² THg+PHg
D2-30	0.210	0.480	7.49	7.97	93.9%	7.9770	94.0%
D2-40	0.300	0.450	8.27	8.72	94.8%	8.7270	94.8%
OH mean	0.255	0.465	7.88	8.35	94.3%	8.35	94.4%
OH Precision, %RPD	35.3%	6.5%	9.9%	9.0%	0.92%	9.0%	0.91%
Accuracy as % recovery	NA	65.2%	106.0%	103.8%	102.2%	103.7%	102.2%

COAL FLUEGAS MATRIX WITH HIGH LEVELSPIKES

COAL FLUEGAS MATRIX WITH HIGH LEVEL SPIKES										Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result			
RESULT	PHg	KCLA	KCLB	ICA	T-Vol		[pHg]	[Hg ⁰]	[Hg ⁺²]	THg	%Hg ⁺²	THg+PHg	%Hg ⁺²
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter		ug/m ³	ug/m ³	ug/m ³	ug/m ³		ug/m ³	
FMS-1-031700	nc	820.9	63.4	245.0	26.6		nc	9.18	33.2	42.4	78.3%	42.39	78.3%
FMS-2-031700	nc	800.2	129.0	237.0	26.6		nc	8.88	34.9	43.8	79.7%	43.79	79.7%
FMS-3-031700	nc	809.2	14.6	214.3	27.3		nc	7.84	30.2	38.0	79.3%	38.06	79.4%
FMS-4-031700	nc	823.4	67.1	256.9	27.4		nc	9.37	32.5	41.9	77.6%	41.95	77.6%
FMS-5-031700	nc	870.7	18.0	258.7	25.4		nc	10.2	35.0	45.2	77.4%	45.24	77.5%
FMS-6-031700	nc	921.9	12.2	234.6	27.2		nc	8.62	34.4	43.0	79.9%	43.01	80.0%
FMS-7-031700	nc	831.5	12.7	191.6	27.0		nc	7.08	31.3	38.3	81.5%	38.36	81.5%
					Flowrate RSD	2.56%							

EERC Run 16

3/17/2000-10:06

n=8

Bitcoal BH with spikes
See MDL-C Calculation
Quads No Tests

FMSS Mean

STDEV

FMSS Precision

NA	8.74	33.1	41.8	79.2%	41.8	79.3%
NA	1.02	1.86	2.69	1.5%	2.69	1.5%
NA	11.7%	5.6%	6.4%	1.9%	6.4%	1.9%

Ontario Hydro Simultaneous Result									
OH SAMPLE ID	[pHg]	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³	%Hg ⁺² THg+PHg		
D9-1o	0.030	7.64	36.6	44.2	82.7%	44.24	82.7%		
D9-2o	0.020	10.18	38.8	49.0	79.2%	49.02	79.2%		
OH mean	0.025	8.91	37.7	46.6	80.9%	46.6	81.0%		
OH Precision, %RPD	40.0%	28.5%	5.9%	10.3%	4.3%	10.3%	4.3%		
Accuracy as % recovery	NA	98.1%	87.7%	89.7%	97.9%	89.7%	97.9%		

COAL FLUEGAS MATRIX MID LEVEL FLOWRATE TESTS

RESULTS							
RESULT	PHg	KCLA	KCLB	ICA	T-Vol	Flowrate	
FMS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter	slpm	
FMS-1-030800	inval	88.81	0.35	5.79	9.1	0.22	
FMS-2-030800	11.2	178.9	1.37	12.04	23.6	0.44	
FMS-3-030800	inval	234.2	0.78	16.56	35.1	0.44	
FMS-4-030800	13.8	199.2	0.35	19.61	24.4	0.57	
							Flowrate, RSD 33.9%
EERC Run 3 n=4	3/8/2000-11:37 Bit-coal ESP no spikes See Quad Flowrate Test Mid Level		FMSS Mean STDEV FMSS Precision		0.516 0.066 12.8% 0.579 0.181 31.3% 7.49 0.74 9.9%		
Ontario Hydro Simultaneous Result							
OH SAMPLE ID	[pHg]	[Hg ⁰]	[Hg ⁺²]	THg	%Hg ⁺²	THg+PHg	%Hg ⁺²
D2-1o	na	0.510	8.98	9.49	84.7%	10.60	94.6%
D2-2o	1.70	0.560	8.37	8.93	83.4%	10.04	93.7%
OH mean	1.70	0.535	8.68	9.21	84.1%	10.32	94.2%
OH Precision, %RPD	NA	9.3%	7.0%	6.1%	1.6%	5.4%	1.0%
Accuracy as % recovery							99.0%

COAL FLUEGAS MATRIX MID LEVEL TEMPERATURE TESTS

COAL FLUEGAS MATRIX MID LEVEL TEMPERATURE TESTS														
RESULT	PHg	KCLA	KCLB	ICA	T-Vol	Temp	[pHg]	[Hg ⁰]	[Hg ⁺²]	Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result				
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr. liter	deg C	ug/m ³	ug/m ³	ug/m ³	THg	THg+PHg	%Hg ⁺²	THg+PHg	%Hg ⁺²
FMS-5-031500	nc	217.7	0.089	3.03	26.0	75.7	nc	0.10	8.39	8.49	98.7%	8.50	98.8%	98.8%
FMS-6-031500	nc	243.6	0.036	5.88	26.2	88.4	nc	0.21	9.31	9.52	97.7%	9.53	97.8%	97.8%
FMS-7-031500	nc	215.3	0.191	3.09	26.3	96.4	nc	0.10	8.19	8.29	98.6%	8.30	98.8%	98.8%
FMS-8-031500	nc	250.1	0.347	4.54	26.4	105.7	nc	0.16	9.49	9.65	98.3%	9.66	98.4%	98.4%
Floware, RSD Temp, RSD														
0.7%														
13.9%														
EERC Run 12 n=4	3/15/2000-13:55							NA	0.142	8.84	8.99	98.3%	9.00	98.4%
	Bitcoal BH no spikes							NA	0.052	0.65	0.69	0.46%	0.69	0.47%
	See Quad Temperature							NA	36.3%	7.3%	7.7%	0.5%	7.7%	0.5%
	Test Mid Level													
Ontario Hydro Simultaneous Result														
OH SAMPLE ID							[pHg]	[Hg ⁰]	[Hg ⁺²]	THg	THg+PHg	%Hg ⁺²	THg+PHg	THg+PHg
D7-3o							0.010	0.350	9.63	9.98	9.99	96.4%	9.99	96.5%
D7-4o							0.010	0.370	10.5	10.9	10.89	96.5%	10.89	96.6%
OH mean							0.010	0.360	10.1	10.4	10.4	96.5%	10.4	96.5%
OH Precision, %RPD							0.0%	5.6%	8.74%	8.6%	8.6%	0.12%	8.6%	0.1%
Accuracy														
as % recovery							NA	39.6%	87.8%	86.1%	101.9%	86.2%	102.0%	102.0%

COAL FLUEGAS MATRIX HIGH LEVEL TEMPERATURE TESTS

COAL FLUEGAS MATRIX HIGH LEVEL TEMPERATURE TESTS																											
RESULT		PHg		KCLA		KCLB		ICA		T-Vol		Temp		Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result													
FMS SAMPLE ID		ng/trap		ng/trap		ng/trap		ng/trap		corr., liter		deg C		[pHg]		[Hg ¹]		[Hg ¹²]		THg		%Hg ⁻²		THg+PHg		%Hg ⁻²	
FMS-1-031600		nc		819.0		15.3		215.6		26.5		75.3		nc		8.10		31.4		39.5		79.5%		39.55		79.5%	
FMS-2-031600		nc		711.1		14.9		220.0		26.4		86.7		nc		8.33		27.5		35.9		76.7%		35.89		76.8%	
FMS-3-031600		nc		732.2		6.89		170.6		26.3		96.6		nc		6.47		28.1		34.6		81.2%		34.58		81.3%	
FMS-4-031600		nc		650.1		61.3		216.7		26.4		105.9		nc		8.20		27.0		35.2		76.6%		35.18		76.7%	
Floware, RSD Temp, RSD 0.4% 14.5%																											
EERC Run 13 3/16/2000-9:23 n=4		Bitcoal BH with spikes												7.78		28.5		36.3		78.5%		36.30		78.6%			
		See Quad Temperature Test High Level												0.874		2.00		2.23		2.23%		2.23		2.23%			
														11.2%		7.02%		6.15%		2.8%		6.1%		2.84%			
														NA													
Ontario Hydro Simultaneous Result																											
OH SAMPLE ID		[pHg]		[Hg ⁰]		[Hg ⁻²]		THg		%Hg ⁻²		THg+PHg		%Hg ⁻²													
D8-1o		0.02		8.23		30.0		38.2		78.4%		38.23		78.5%													
D8-2o		0.02		8.67		33.7		42.4		79.5%		42.41		79.5%													
OH mean		0.02		8.45		31.9		40.3		79.0%		40.3		79.0%													
OH Precision, %RPD		0.0%		5.2%		11.7%		10.4%		1.4%		10.4%		1.4%													
Accuracy as % recovery		NA		92.0%		89.5%		90.0%		99.4%		90.0%		99.4%													

COAL FLUEGAS MATRIX HIGH LEVEL FLOWRATE TESTS

[illegible]

CLEAN NATURAL GAS FLUEGAS MATRIX WITH Hg° SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-6-030700	nc	0.532	0.184	389.2	29.6
FMS-7-030700	nc	0.307	0.020	392.1	30.1
FMS-8-030700	nc	1.043	0.020	302.1	24.5
				Flowrate RSD	11.0%

EERC Run 1
3/7/2000-13:35
n=3
Natural Gas
Hg° spikes

Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result						
	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺² THg+PHg	%Hg ⁰ THg+PHg
	na	13.1	0.0214	13.2	0.16%	0.16%
	na	13.0	0.0080	13.0	0.06%	0.06%
	na	12.3	0.0406	12.4	0.33%	0.33%

FMSS Mean NA 12.8 0.0233 12.8 0.18% 12.9 0.18% 99.66%
STDEV NA 0.44 0.016 0.428 0.13% 0.43 0.13% 0.139%
FMSS Precision NA 3.45% 70.2% 3.34% 73.1% 3.3% 73.1% 0.140%

Ontario Hydro Simultaneous Result						
OH SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺² THg+PHg	%Hg ⁰ THg+PHg
D1-1o	0.02	10.05	0.23	10.3	2.2%	2.2%
na	na	na	na	na	na	na

OH mean 0.02 10.05 0.23 10.3 2.2% 2.2% 97.57%

OH Precision, %RPD NA NA NA NA NA NA NA

Accuracy as % recovery	NA	NA	NA	NA	NA	NA
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CLEAN NATURAL GAS FLUEGAS MATRIX WITH Hg⁺² SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-10-030700	nc	381.7	0.000	66.8	27.7
FMS-11-030700	nc	403.4	0.123	61.0	28.6
FMS-12-030700	nc	371.9	0.020	46.5	25.6
				Flowrate RSD	5.6%

EERC Run 2
3/7/2000-16:40
n=3
Natural Gas
Hg⁺² spikes

Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result						
	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺² THg+PHg	%Hg ⁰ THg+PHg
	na	2.40	13.8	16.2	76.1%	85.2%
	na	2.12	14.1	16.2	77.7%	86.9%
	na	1.80	14.5	16.3	79.5%	89.0%

FMSS Mean NA 2.10 14.1 16.2 77.7% 18.2 87.0%
STDEV NA 0.30 0.38 0.08 1.73% 0.077 1.90%
FMSS Precision NA 14.2% 2.65% 0.48% 2.23% 0.43% 2.18%

Ontario Hydro Simultaneous Result						
OH SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺² THg+PHg	%Hg ⁰ THg+PHg
D1-2o	1.94	2.11	6.38	8.49	61.2%	75.1%
na	na	na	na	na	na	na

OH mean 1.94 2.11 6.38 8.49 61.2% 75.1%

OH Precision, %RPD NA NA NA NA NA NA

Accuracy as % recovery	NA	NA	NA	NA	NA	NA
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COAL FLUEGAS MATRIX MID LEVEL NO SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-1-031000	2.65	193.6	0.426	11.0	25.9
FMS-2-031000	1.52	206.5	1.35	7.57	25.3

Flowrate RSD 1.6%

EERC Run 5
3/10/2000-16:24
n=2
Bitcoal ESP
No Spikes

FMSS Mean	0.079	0.347	7.86	8.20	93.1%	8.44	95.7%
STDEV	0.030	0.089	0.50	0.42	1.4%	0.42	1.3%
FMSS Precision	53.5%	36.4%	9.09%	7.16%	2.12%	6.97%	1.93%

Ontario Hydro Simultaneous Result							
OH SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³	%Hg ⁺² THg+PHg
D4-10	0.370	0.46	6.63	7.09	90.5%	7.32	93.5%
D4-20	0.400	0.46	6.99	7.45	91.0%	7.68	93.8%
OH mean	0.385	0.46	6.81	7.27	90.8%	7.50	93.7%
OH Precision, %RPD	7.8%	0.0%	5.3%	5.0%	0.5%	4.8%	0.33%
Accuracy as % recovery	20.6%	75.4%	115.4%	112.9%	102.6%	112.5%	102.2%

COAL FLUEGAS MATRIX WITH HIGH LEVEL SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-1-031300	15.1	745.2	63.5	87.8	25.1
FMS-2-031300	inval	776.2	43.7	120.7	25.1

Flowrate RSD 0.1%

EERC Run 6
3/13/2000-9:20
n=2
Bitcoal ESP
With Spikes

FMSS Mean	0.60	4.14	32.5	36.6	87.3%	37.2	88.7%
STDEV	NA	0.924	0.291	1.22	2.1%	1.22	2.2%
FMSS Precision	NA	31.6%	1.27%	4.70%	3.4%	4.6%	3.43%

Ontario Hydro Simultaneous Result							
OH SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³	%Hg ⁺² THg+PHg
D5-10	0.66	4.67	30.4	35.07	85.3%	35.65	86.7%
D5-20	0.48	7.02	25.5	32.54	77.0%	33.12	78.4%
OH mean	0.57	5.85	28.0	33.8	81.2%	34.4	82.6%
OH Precision, %RPD	31.6%	40.2%	17.5%	7.5%	10.1%	7.4%	10.0%
Accuracy as % recovery	105.1%	70.8%	116.1%	108.3%	107.6%	108.1%	107.5%

COAL FLUEGAS MATRIX WITH HIGH LEVEL SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-3-031300	3.3	629.8	6.39	170.6	25.7
FMS-4-031300	2.2	705.7	7.49	197.1	25.7
				Flowrate RSD	0.1%

EERC Run 7
n=2
3/13/2000-14:50
Bitcoal ESP
With Spikes

Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result						
	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³
	0.125	6.63	24.8	31.4	78.4%	31.6
	0.082	7.66	27.8	35.4	77.9%	35.6

FMSS Mean 0.104 7.15 26.3 33.4 78.2% 33.6 78.6%
STDEV 0.030 0.72 2.10 2.83 42.5% 2.83 42.6%
FMSS Precision 41.0% 14.3% 11.3% 12.0% 0.58% 11.9% 0.65%

Ontario Hydro Simultaneous Result						
OH SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³
D5-30	0.290	6.97	24.8	31.8	77.6%	32.00
D5-40	0.310	6.64	32.6	39.3	82.7%	39.47
OH mean	0.300	6.81	28.7	35.5	80.1%	35.7
OH Precision, %RPD	6.7%	4.8%	27.1%	21.0%	6.3%	20.9%
						6.2%

Accuracy
as % recovery 34.6% 105.0% 91.5% 94.0% 97.5% 94.1% 97.6%

COAL FLUEGAS MATRIX WITH HIGH LEVEL SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-6-031300	23.0	655.9	6.2	86.9	25.1
FMS-7-031300	inval	522.1	156.7	181.4	25.2
				Flowrate RSD	0.3%

EERC Run 8
3/13/2000-18:53
Bitcoal ESP
With Spikes

Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result						
	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³
	0.914	3.45	26.4	29.9	86.2%	30.62
	nc	7.18	26.9	34.1	77.2%	34.89

FMSS Mean 0.91 5.32 26.7 32.0 81.7% 32.8 83.7%
STDEV NA NA 0.38 3.02 40.2% 3.02 40.6%
FMSS Precision NA NA 2.0% 13.3% 11.0% 13.0% 11.3%

Ontario Hydro Simultaneous Result						
OH SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³
D5-50	0.66	7.56	23.8	31.40	74.1%	32.17
D5-60	0.60	7.66	30.6	38.21	78.4%	38.98
OH mean	0.63	7.61	27.2	34.8	76.2%	35.6
OH Precision, %RPD	9.5%	1.3%	24.7%	19.6%	5.6%	19.1%
						5.2%

Accuracy
as % recovery 145.0% 69.9% 98.1% 91.9% 107.2% 92.1% 107.4%

COAL FLUEGAS MATRIX WITH HIGH LEVEL SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-1-031400	83.2	448.9	0.22	12.7	16.7
FMS-2-031400	63.0	503.8	1.26	12.8	23.6
FMS-3-031400	95.9	596.7	30.3	16.2	27.3

Flowrate RSD 23.9%

EERC Run 9

3/14/2000-10:30
n=3
Bitcoal ESP - heavy particulate
With Spikes

Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result						
FMSS SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³
FMS-1-031400	4.99	0.746	26.9	27.7	85.3%	31.55
FMS-2-031400	2.66	0.528	21.4	21.9	82.9%	25.78
FMS-3-031400	3.51	0.579	23.0	23.6	83.7%	27.44

FMSS Mean	3.72	0.618	23.8	24.4	84.0%	28.3
STDEV	1.18	0.114	2.85	2.97	1.24%	2.97
FMSS Precision	31.6%	18.5%	12.0%	12.2%	1.47%	10.5%

Ontario Hydro Simultaneous Result

OH SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³
D6-10	1.21	0.91	21.6	23.7	78.2%	27.59
D6-20	6.89	1.26	24.1	32.3	66.7%	36.14

OH mean	4.05	1.09	22.8	28.0	72.5%	31.9
OH Precision, %RPD	140.2%	32.3%	11.0%	30.6%	15.9%	26.8%

Accuracy

as % recovery	91.9%	56.9%	104.0%	87.1%	115.9%	88.7%
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COAL FLUEGAS MATRIX WITH HIGH LEVEL SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMSS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-5-031400	138.8	420.7	0.736	20.6	20.8
FMS-6-031400	143.3	168.2	0.399	8.85	12.2
FMS-7-031400	128.9	272.4	0.337	16.5	21.4

Flowrate RSD 28.3%

EERC Run 10

3/14/2000-16:00
n=3
Bitcoal ESP - heavy particulate
With Spikes

Frontier's Fluegas Mercury Sorbent Speciation (FMSS) Result						
FMSS SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³
FMS-5-031400	6.68	0.98	20.3	21.3	68.1%	29.77
FMS-6-031400	11.7	0.71	13.8	14.5	59.9%	23.02
FMS-7-031400	6.01	0.75	12.7	13.5	57.9%	22.00

FMSS Mean	8.14	0.81	15.6	16.42	62.0%	24.93
STDEV	3.13	0.14	4.09	4.22	5.4%	4.22
FMSS Precision	38.4%	17.5%	26.2%	25.7%	8.75%	16.9%

Ontario Hydro Simultaneous Result

OH SAMPLE ID	[pHg] ug/m ³	[Hg ⁰] ug/m ³	[Hg ⁺²] ug/m ³	THg ug/m ³	%Hg ⁺²	THg+PHg ug/m ³
D6-30	10.3	1.58	19.7	21.3	66.1%	29.80
D6-40	7.53	1.9	23.6	25.4	69.5%	33.96

OH mean	8.89	1.72	21.6	23.4	67.8%	31.9
OH Precision, %RPD	30.6%	15.7%	18.0%	17.8%	4.9%	13.1%

Accuracy

as % recovery	91.6%	47.4%	72.1%	70.3%	91.4%	78.2%
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COAL FLUEGAS MATRIX MID LEVEL NO SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-1-031500	nc	236.0	0.242	2.37	26.1
FMS-2-031500	nc	269.4	0.039	2.88	26.1
FMS-3-031500	nc	243.6	0.574	2.30	27.3

Flowrate RSD 2.7%

EERC Run 11

3/15/2000 -9:40
n=3
Bitcoal BH
No Spikes

FMSS Mean	NA	0.0798	9.45	9.53	98.7%	9.57	99.2%
STDEV	NA	0.014	0.767	0.781	0.05%	0.78	0.074%
FMSS Precision	NA	17.1%	8.12%	8.20%	0.05%	8.2%	0.08%

Ontario Hydro Simultaneous Result

OH SAMPLE ID	[pHg]	[Hg ¹]	[Hg ²]	THg	%Hg ⁻²	THg+PHg	%Hg ⁻²
	ug/m ³	ug/m ³	ug/m ³	ug/m ³		ug/m ³	

D7-10	0.060	0.400	9.78	10.18	95.7%	10.22	96.1%
D7-20	0.020	0.470	10.7	11.15	95.4%	11.19	95.8%

OH mean	0.040	0.435	10.2	10.7	95.6%	10.7	95.9%
	0.028	0.049	0.64	0.69	0.18%	0.69	0.20%
OH Precision, %RPD	100.0%	16.1%	8.8%	9.1%	0.26%	9.1%	0.30%

Accuracy as % recovery	NA	18.3%	92.3%	89.3%	103.3%	89.4%	103.4%
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OH Precision, %RPD

COAL FLUEGAS MATRIX WITH HIGH LEVEL SPIKES

RESULT	PHg	KCLA	KCLB	ICA	T-Vol
FMS SAMPLE ID	ng/trap	ng/trap	ng/trap	ng/trap	corr., liter
FMS-5-031600	nc	699.5	9.80	246.1	23.5
FMS-6-031600	nc	812.6	6.76	268.5	25.9
FMS-7-031600	nc	599.5	6.10	227.2	26.3

Flowrate RSD 6.0%

EERC Run 14

3/16/2000-12:31
n=3
Bitcoal BH
With Spikes

FMSS Mean	NA	9.8	28.3	38.1	74.1%	38.1	74.1%
STDEV	NA	1.03	4.62	5.63	1.31%	5.63	1.30%
FMSS Precision	NA	10.5%	16.3%	14.8%	1.76%	14.8%	1.75%

Ontario Hydro Simultaneous Result

OH SAMPLE ID	[pHg]	[Hg ¹]	[Hg ²]	THg	%Hg ⁻²	THg+PHg	%Hg ⁻²
	ug/m ³	ug/m ³	ug/m ³	ug/m ³		ug/m ³	

D8-30	na	8.54	29.9	38.4	77.7%	38.43	77.8%
D8-40	0.02	9.70	32.4	42.1	76.9%	42.13	77.0%

OH mean	0.02	9.12	31.1	40.3	77.3%	40.3	77.4%
OH Precision, %RPD	NA	12.7%	8.2%	9.2%	1.03%	9.2%	1.04%

Accuracy as % recovery	NA	107.6%	90.8%	94.6%	95.8%	94.6%	95.8%
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